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VOL. II

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WATTS'

DICTIONARY OF CHEMISTRY

REVISED AND ENTIRELY REWRITTEN

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ASSISTED BY EMINENT CONTRIBUTORS

IN FOUR VOLUMES

VOL. II.

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INTRODUCTION

TO THE ARTICLES RELATING TO ORGANIC CHEMISTRY.

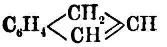
In the present volume the nomenclature is the same as that adopted in the first volume. It has been explained in the Introduction to that volume, pp. viii–xiv. Thus, to take a single instance, the products of condensation between hydrazines and ketonic compounds are still called hydrazides, although Emil Fischer has, since the publication of the last volume, changed their name to hydrazones. Even supposing the latter name to be preferable, its abrupt introduction would greatly confuse the nomenclature by depriving it of uniformity.

Since the publication of the first volume I have been assisted in the work of reading and making abstracts of original memoirs by Drs. T. A. Lawson and Samuel Rideal, Messrs. J. Wilkie, J. T. Norman, V. H. Veley, G. N. Huntly, S. H. Collins, Dr. G. McGowan, and Mr. D. A. Louis. I have also been ably assisted by Mr. Arthur G. Green in the work of revising the proof sheets. I have great pleasure in thanking these gentlemen for the energetic and efficient manner in which they have carried out their share of the work.

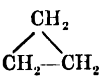
H. Forster Morley.

Nomenclature of Ring Formulæ.

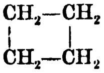
Hydrocarbons.



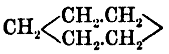
$C_6H_4<\begin{matrix}CH_2\\CH\end{matrix}>CH$ *Indonaphthene.*



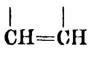
Trimethylene.



Tetramethylene.

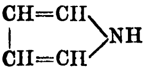


$CH_2<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}>$ *Pentamethylene.*

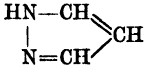


Tetramethenyl.

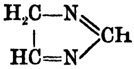
Nitrogen ring compounds.



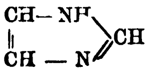
Pyrrole or *Pyrrol.*



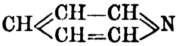
Pyrazole.



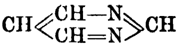
Metapyrazole.



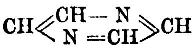
Glyoxaline.



$CH<\begin{matrix}CH-CH\\CH=CH\end{matrix}>N$ *Pyridine.*

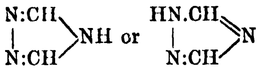


$CH<\begin{matrix}CH-N\\CH=N\end{matrix}>CH$ *Pyrimidine.*

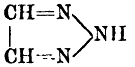


$CH<\begin{matrix}CH-N\\N=CH\end{matrix}>CH$ *Pyrazine.*

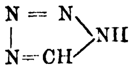
Nitrogen ring compounds—cont.



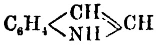
Triazole.



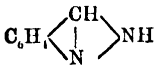
Osotriazole.



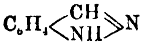
Tetrazole.



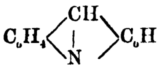
$C_6H_4{<}\genfrac{}{}{0pt}{}{CH}{NH}{>}CH$ *Indole.*



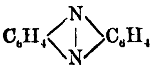
Indazine.



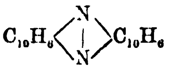
$C_6H_4{<}\genfrac{}{}{0pt}{}{CH}{NH}{>}N$ *Pseudo-indazine.*



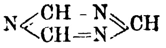
Acridine.



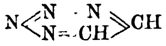
Phenazine.



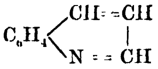
Naphthazine.



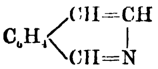
$N{<}\genfrac{}{}{0pt}{}{CH-N}{CH=N}{>}CH$ *Triazoline.*



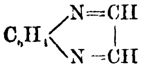
$N{<}\genfrac{}{}{0pt}{}{N-N}{N=CH}{>}CH$ *Osotetrazole.*



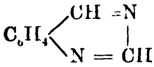
Quinoline.



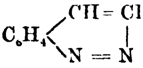
Isoquinoline.



Quinoxaline.

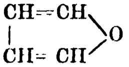


Quinazoline.

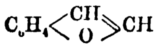


Cinnoline.

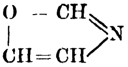
Oxygen ring compounds.



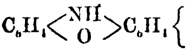
Furfurane.



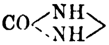
$C_6H_4{<}\genfrac{}{}{0pt}{}{CH}{O}{>}CH$ *Coumarone.*



Oxazole.

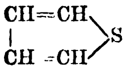


$C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{O}{>}C_6H_4$ *Phenazoxine* or *Di phenyl-oxazine.*

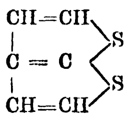


$CO{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}$ *Carbizine.*

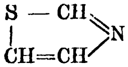
Sulphur ring compounds.



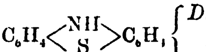
Thiophene.



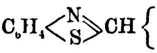
Thiophthene.



Thiazole.



$C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{S}{>}C_6H_4$ *Di-phenyl-thiazine* (*thiodiphenylamine* or *Imido-di-phenyl sulphide*).



$C_6H_4{<}\genfrac{}{}{0pt}{}{N}{S}{>}CH$ *Methenyl-amido-phenyl-mercaptan.*

In many of the above formulæ the exact structure is not known; alternative ways of writing some of them will be found in vol. i. p. xii.

INITIALS OF SPECIAL CONTRIBUTORS.

H. B.	HARRY BAKER, Esq., F.C.S., *Chemist to the Aluminium Company, Oldbury.* Contributes Crystallisation.
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D. H.	DAVID HOWARD, Esq. Contributes Cinchona bark.
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Articles by Mr. MUIR are initialed M. M. P. M.

Unsigned Articles are by Dr. MORLEY.

ABBREVIATIONS

I. JOURNALS AND BOOKS.

When an author has been mentioned in an article, he is usually referred to thereafter in that article by his initial only.

A.	Liebig's Annalen der Chemie.
A. A.	Annales de la Sociedad Cientifica Argentina.
A. Ch.	Annales de Chimie et de Physique.
P. Am. A.	Proceedings of the American Academy of Arts and Sciences.
Am.	American Chemical Journal.
Ann. M.	Annales des Mines.
Am. S.	American Journal of Science.
A. C. J.	Journal of the American Chemical Society.
Am. Ch.	American Chemist.
Am. J. Pharm.	American Journal of Pharmacy.
An.	The Analyst.
A. Ph. S.	Proceedings of the American Philosophical Society.
Ar. N.	Archives néerlandaises—The Hague.
Acad.	Mémoires de l'Académie des Sciences.
Ar. Ph.	Archiv der Pharmacie.
Ar. Sc.	Archives des Sciences phys. et nat.
B.	Berichte der deutschen chemischen Gesellschaft.
B. A.	Reports of the British Association.
Bl.	Bulletin de la Société chimique de Paris.
B. B.	Berliner Akademie-Berichte.
B. C.	Biedermann's Centralblatt für Agricultur-Chemie.
B. J.	Berzelius' Jahresberichte.
B. M.	Berliner Monatsberichte.
C.S. Mem.	Memoirs of the Chemical Society of London.
C. J.	Journal of the Chemical Society of London.
C.J. Proc.	Proceedings of the Chemical Society of London.
C. N.	Chemical News.
C. R.	Comptes-rendus hebdomadaires des Séances de l'Académie des Sciences—Paris.
C. C.	Chemisches Central-Blatt.
D. P. J.	Dingler's polytechnisches Journal.
Fr.	Fresenius' Zeitschrift fur analytische Chemie.
G.	Gazzetta chimica italiana.
G. A.	Gilbert's Annalen der Physik und Chemie.
H.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
I.	Proceedings of the Royal Irish Academy.
J.	Jahresbericht uber die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
J. C. T.	Jahresbericht für Chemische Technologie.
J. M.	Jahrbuch für Mineralogie.
J. de Ph.	Journal de Physique et des Sciences accessoires.
J. Ph.	Journal de Pharmacie et de Chimie.
J. pr.	Journal für praktische Chemie.
J. Th.	Jahresbericht über Thierchemie.
J. R.	Journal of the Russian Chemical Society.
J. Z.	Jenaische Zeitschrift für Medicin und Naturwissenschaft.
L. V.	Landwirthschaftliche Versuchs-Stationen.
M.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
M. S.	Le Moniteur Scientifique.
Mém. S. d'A.	Mémoires de la Société d'Arcueil.
Mém. B.	Mémoires couronnés par l'Académie de Bruxelles.

N.	Nature.	
N.Ed.P.J.	New Edinburgh Philosophical Journal.	
N. J. P.	Neuer Jahresbericht der Pharmacie.	
N. R. P.	Neues Repertorium fur die Pharmacie.	
N. J. T.	Neues Journal von Trommsdorff.	
P. M.	Philosophical Magazine.	
P.	Poggendorff's Annalen der Physik und Chemie.	
P. B.	Beiblätter zu den Annalen der Physik und Chemie.	
Pf.	Pflüger's Archiv fur Physiologie.	
Pr. E.	Proceedings of the Royal Society of Edinburgh.	
Ph.	Pharmaceutical Journal and Transactions.	
Ph. C.	Pharmaceutisches Central-Blatt.	
Pr.	Proceedings of the Royal Society.	
P. R. I.	Proceedings of the Royal Institution of Great Britain.	
P. Z.	Pharmaceutische Zeitschrift fur Russland.	
R. T. C.	Recueil des travaux chimiques des Pays-Bas.	
R. P.	Repertorium fur die Pharmacie.	
Q. J. S.	Quarterly Journal of Science.	
S.	Schweigger's Journal der Physik.	
Scher. J.	Scherer's Journal der Chemie.	
S. C. I.	Journal of the Society of Chemical Industry.	
Sitz. W.	Sitzungsberichte der K. Akademie zu Wien.	
T. or *Tr.*	Transactions of the Royal Society.	
T. E.	Transactions of the Royal Society of Edinburgh.	
W.	Wiedemann's Annalen der Physik und Chemie.	
W. J.	Wagner's Jahresbericht.	
Z.	Zeitschrift für Chemie.	
Z. B.	Zeitschrift fur Biologie.	
Z. f. d. g. Naturwiss.	Zeitschrift für die gesammten Naturwissenschaften.	
Z. K.	Zeitschrift fur Krystallographie und Mineralogie.	
Z. P. C.	Zeitschrift für physikalische Chemie.	
Bn.	Handbuch der organischen Chemie: von F. Beilstein, 2te Auflage.	
E. P.	English Patent.	
G. P.	German Patent.	
Gm.	Gmelin's Handbook of Chemistry—English Edition.	
Gm.-K.	Gmelin-Kraut: Handbuch der anorganischen Chemie.	
Gerh.	Traité de Chimie organique: par Charles Gerhardt.	
K.	Lehrbuch der organischen Chemie: von Aug. Kekulé.	
G. O.	Graham-Otto: Lehrbuch der anorganischen Chemie [5th Ed.]	
Stas. Rech.	Stas' Recherches, &c.	Aronstein's German translation is referred to as *Chem. Proport.*
Stas. Nouv. R.	Stas' Nouvelles Recherches, &c.	
Th.	Thomsen's Thermochemische Untersuchungen.	

II. Terms and Quantities, &c., frequently used.

Aq.	Water; e.g. NaOHAq means an aqueous solution of caustic soda.
aq.	18 parts by weight of water.
A′ A″ A‴	Residues of mono-, di-, and tri-basic acids. Thus, in describing the salts of a monobasic acid NaA′, CaA'_2, AlA'_3 may be written, HA′ standing for the acid. For a dibasic acid we should write Na_2A'', CaA″, $Al_2A''_3$ &c.
B′ B″ etc.	Stand for bases of the ammonia type, in describing their salts. Thus the hydrochloride would be B′HCl or B″2HCl, according as the base is monacid or diacid, &c.
conc.	Concentrated.
dil.	Dilute.
g.	gram.
mgm.	milligram.
mm.	millimetre.
mol.	molecule.
oil.	liquid, nearly, or quite, insoluble in water.
pp.	precipitate.
to ppt.	to precipitate.
png.	precipitating.
ppd.	precipitated.

sol.	soluble in.
insol.	insoluble in.
v. e. sol.	very easily ⎫
v. sol.	very ⎪
m. sol.	moderately ⎬ soluble in.
sl. sol.	slightly ⎪
v. sl. sol.	very slightly ⎭
v.	see.
cf.	compare.
c.	about.
[°]	a melting-point.
(°)	a boiling-point.
H.	Hardness (of minerals).
At. w.	Atomic weight.
Mol. w. or M. w.	Molecular weight.
D.	Density.
cor.	corrected.
uncor.	uncorrected.
i.V.	in vapour.
V.D.	vapour-density, *i.e.* density of a gas compared with hydrogen or air
S.G.	Specific gravity compared with water.
S.G. $\frac{10}{0}$	,, ,, at 10° compared with water at 0°.
S.G. $\frac{15}{4}$	,, ,, ,, 15° ,, ,, ,, ,, 4°.
S.G. $\frac{12}{}$	,, ,, ,, 12° ; compared with water of which the temperature is not given.
S.H.	Specific heat.
S.H. v.	,, ,, of a gas at constant volume.
S.H. p.	,, ,, ,, ,, ,, pressure.
H.C.	Quantity of heat, in gram-units, produced during the complete combustion of the mass of a solid or liquid body represented by its formula, taken in grams.
H.C. v.	Heat of combustion in gram-units of a gram-molecule of an element or compound, when gaseous, under constant volume.
H.C. p.	The same, under constant pressure.
H.F.	Quantity of heat, in gram-units, produced during the formation of the mass of a solid or liquid body represented by its formula, taken in grams, from the masses of its constituent elements expressed by their formulæ, taken in grams.
H.F. v.	Heat of formation of a gram-molecule of a gaseous compound from the gram-molecules of its elements under constant volume.
H.F. p.	The same, under constant pressure.
H.V.	Heat of vaporisation of a liquid, *i.e.* gram-units of heat required to change a gram-molecule of the liquid compound at B. P. into gas at same temperature and pressure.
T.C.	Thermal conductivity (unit to be stated).
S.V.	Specific volume ; or the molecular weight of a gaseous compound divided by the S.G. of the liquid compound at its boiling-point compared with water at 4°.
S.V.S.	Specific volume of a solid; or the mass of the solid expressed by its formula, taken in grams, divided by its S.G.
E.C.	Electrical conductivity (the unit is stated in each case).
C.E. (10° to 20°)	Coefficient of expansion (between 10° and 20°).
S.	Solubility in water ⎧ of a gas = volume dissolved by 1 volume of water. ⎨ of a liquid or solid = number of grms. dissolved by 100 grms. of water. In both cases the temperature is stated.
S. (alcohol)	,, ,, alcohol ⎩
μ_β	Index of refraction for hydrogen line β.
μ_D, &c.	,, ,, ,, sodium ,, D, &c.
$R_D \frac{15}{0}$	Molecular refraction for sodium light, i.e. index of refraction for line D minus one, multiplied by molecular weight, and divided by S.G. at 15° compared with water at 0°.
R_D	The same ; S.G. being determined at 15°-20° and referred to water at 4°.
R_∞	The same for line of infinite wave-length, index being determined by Cauchy's formula (Bruhl's R_A).
$[\alpha]_D$	Specific rotation for sodium light.
$[\alpha]_j$	,, ,, ,, neutral tint. $[\alpha] = \frac{100}{p} \times \frac{\alpha}{d}$. α = observed rotation for 100 mm. of liquid. d = S.G. of liquid. p = no. of grammes of active substance in 100 grammes of liquid.

M. M.	Molecular magnetic rotatory power $= \frac{m \times \alpha}{d \times \alpha' \times m'}$, where m = molecular weight of the body of S.G. $= d$, $\alpha =$ angle of rotation under magnetic influence, $\alpha' =$ angle of rotation of water under same influence, and $m' =$ molecular weight of water (18)	
Ac . .	Acetyl C_2H_3O.	
Bz . .	Benzoyl C_7H_5O.	
Cy . .	Cyanogen CN.	
Et . .	Ethyl C_2H_5.	in formulæ.
Me .	Methyl CH_3.	
Ph . .	Phenyl C_6H_5.	
Pr . .	Normal Propyl $CH_2.CH_2.CH_3$.	
Pr . .	Isopropyl $CH(CH_3)_2$.	
R, R′ &c.	Alcohol radicles or alkyls.	
prim . .	primary.	
sec . .	secondary.	
tert . .	tertiary.	
n . . .	normal.	
m, o, p .	meta– ortho—para.	
c . . .	consecutive.	
i . . .	irregular.	
s . .	symmetrical.	
u . . .	unsymmetrical.	
ψ . . .	pseudo.	
ν . . .	attached to nitrogen.	
α . . β . . γ . .	Employed to denote that the substituent is attached to a carbon atom which is next, next but one, or next but two, respectively, to the terminal carbon atom. The end to be reckoned from is determined by the nature of the compound. Thus $CH_3.CHBr.CO_2H$ is α-bromopropionic acid.	
ω . . .	denotes that the element or radicle which follows it is attached to a terminal carbon atom.	
α,β,γ, &c.	indicate position in an open chain, only.	
1,2,3, &c.	indicate position in a ring only.	
(α), (β), &c.	Used when α, β, &c. are employed in a sense different from the above, *e.g.* (α)-di-bromo-camphor.	
	Baeyer's Nomenclature:	
(*B.*) . .	benzene ring.	
(*Py.*) . .	pyridine ring. Thus (*B.* 1:3) dichloroquinoline, means a meta-dichloroquinoline in which the chlorine atoms are both in the benzene ring. While (*Py.* 1:3) dichloroquinoline, means a similar body, only the chlorine atoms are in the pyridine ring. The numbers are counted from two carbon atoms which are in different rings, but both united to the same carbon atom.	
(*A.*) . .	denotes the central ring in the molecule of anthracene, acridines, and azines.	
eso- . .	means that the element or radicle it precedes is in a closed ring.	
exo- . .	,, ,, ,, ,, ,, not in a benzene ring.	
allo- . .	denotes isomerism that is not indicated by ordinary formulæ; thus maleic acid may be called *allo*-fumaric acid.	
thio- . .	denotes displacement of oxygen by sulphur.	
sulpho- .	,, the group SO_3H, except in the word sulphocyanide.	
sulphydro-	,, the group SH.	
	Tribromonitrobenzene sulphonic acid [1:2:3:4:5] means that the three bromines occupy positions 1, 2, and 3; the nitro- group the position 4, and the sulpho- group the position 5.	

* Denotes that the formula to which it is affixed has not been determined by analysis. But it by no means follows that formulæ without this mark are those of analysed compounds.

All temperatures are given in degrees Centigrade unless when specially stated otherwise.

Wave-lengths are given in 10^{-7} mm.

Formulæ, when used instead of names of substances, have a qualitative meaning only.

Thomsen's notation is used in thermochemical data.

DICTIONARY OF CHEMISTRY.

CHENOCHOLIC ACID $C_{27}H_{44}O_4$. Formed by boiling taurochenocholic acid, from goose-bile, with baryta-water (Heintz a. Wislicenus, *P.* 108, 547). Amorphous mass (from alcohol or ether), insol. water. Gives Pettenkofer's reaction with H_2SO_4 and sugar. Insol. cold KOHAq, but dissolves on warming, forming a solution that is ppd. by $BaCl_2$ and $CaCl_2$.—BaA'_2 (dried).

CHENOPODINE $C_6H_{13}NO_4$. This base, which occurs in white goosefoot (*Chenopodium album*) (Reinsch, *N. J. P.* 20, 268; 21, 132; 27, 193; *J. pr.* [2] 22, 188), is probably leucine (Gorup-Besanez, *B.* 7, 147).

CHICA. A red dye obtained from the leaves of *Bignonia Chica* growing in South America. The colouring-matter may be extracted by alcohol. It is insol. ether and Na_2CO_3Aq, but sol. NaOHAq. Chromic acid oxidises it to anisic acid (Erdmann, *J. pr.* 71, 198).

CHICORY. The blue blossoms of *Cichorium Intybus* contain a glucoside $C_{32}H_{34}O_{19}$ $4\frac{1}{2}$aq [215°–220°], which may be extracted by dilute alcohol. It crystallises from water, in which it is slightly soluble, in needles. Aqueous alkalis and alkaline carbonates form yellow solutions. Boiling dilute acids split it up into glucose and $C_{20}H_{14}O_9$ [250°–255°], which also occurs in the blossoms. This forms needles, v. sl. sol. boiling water, coloured dark green by Fe_2Cl_6 (Nietzki, *J.* 1876, 851; *Ar. Ph.* [3] 8, 327).

CHICLE ALBAN $C_{10}H_{16}O$. [145°]. S. (alcohol of S.G. ·82) ·66 at 14°. Obtained by extracting chicle gum (Mexican rubber juice), from *Chrysophyllum glycyplacum*, with weak alcohol (Prochazka a. Endemann, *A. C. J.* 1, 50). The mother liquor deposits **chicle fluavil** $C_{20}H_{32}O$ (?); S. (alcohol of S.G. ·82) 2·6 at 13·5°. The residue of the gum, after extracting with alcohol, contains two terpenes and arabin.

CHIN-. Substances beginning with Chin- will be described under the alternative names which begin with Quin-. Thus Chinidine, Chinone, and Chinoline are described as Quinidine, Quinone, and Quinoline.

CHIRATIN $C_{26}H_{48}O_{15}$. Extracted by dilute alcohol from the stalks of *Ophelia chirata* (Höhn, *Ar. Ph.* [2] 139, 213). Resinous mass, decomposed by hot dilute HCl into ophelic acid and morphous chiratogenin $C_{13}H_{24}O_3$.

CHITENIDINE $C_{19}H\ N_2O_4$. Formed by oxidation of quinidine with $KMnO_4$. Thin plates (containing 2aq). Sol. alkalis and hot water, sl. sol. alcohol.—$B''H_2SO_4$ 3aq: white prisms.—$B''H_2Cl_2PtCl_4$ 3aq: large orange-red needles (Forst a. Böhringer, *B.* 15, 1659).

CHITENINE $C_{19}H_{22}N_2O_4$. Prepared by oxidation of quinine with $KMnO_4$. White prisms (containing 4aq). Insol. alcohol and ether, sl. sol. water. Very weak base.—$B_2(H_2SO_4)_3$ 15aq: fine needles.—$BH_2Cl_2PtCl_4$ 3aq (Skraup, *B.* 12, 1104).

CHITIN *v.* Proteids, *Appendix C.*

CHLORAL C_2HCl_3O *i.e.* $CCl_3.CHO$. *Tri-chloro-acetic aldehyde.* Mol. w. 147·5. [c. −75°] (Berthelot, *Bl.* [2] 29, 3). (98° cor.) (Perkin); (97·2°) (Thorpe, *C. J.* 37, 191). V.D. 5·13. S.G. $\frac{9}{9}$ 1·5292 (Perkin, *C. J.* 51, 808); $\frac{20}{4}$ 1·5121 (Brühl, *A.* 203, 11); $\frac{0}{4}$ 1·5417 (Pa.). C.E. (0°–10°) ·001123; (0°–100°) ·001295 (Laura Passavant, *C. J.* 39, 53). μ_D 1·4623. R_∞ 43·06. M.M. 6·591 at 16° (Perkin). S.V. 107·4.

Formation.—1. By the action of chlorine on aqueous aldehyde (Pinner, *B.* 4, 256; Wurtz a. Vogt, *Z.* 1871, 679).—2. From tri-chloro-acetal and H_2SO_4 at 150° (Paterno, *A.* 150, 256; *Z.* [2] 4, 733).—3. By distilling starch or sugar with HCl and MnO_2 (Städeler, *A.* 61, 101).—4. By distilling tetra-chloro-ether, $CCl_3.CHCl(OEt)$, with H_2SO_4 (W. a. V.).

Preparation.—Chlorine gas is passed into absolute alcohol, which must be cooled at first, but afterwards may be heated gradually to boiling. The crystalline chloral alcoholate formed is decomposed by shaking with H_2SO_4 and the liquid chloral rectified (Liebig, *A.* 1, 189; Dumas, *A. Ch.* [2] 56, 125; Muller a. Paul, *B.* 2, 541; Thomsen, *Z.* [2] 6, 156; Roussin, *Z.* [2] 6, 96; Personne, *C. R.* 69, 1363; Paul, *Ph.* [3] 1, 621; *C. J.* 24, 134). By-products are ethylidene chloride, ethylene chloride, and chloro-ethylene chloride (115°). The chlorination is promoted by the presence of 5 p.c. Fe_2Cl_6 (Page, *D. P. J.* 252, 343. *V.* also Chloral hydrate).

Theory of the process.—Chlorine oxidises alcohol to aldehyde, this combines with alcohol forming acetal $CH_3CH(OEt)_2$, which is then converted into tri-chloro-acetal $CCl_3CH(OEt)_2$ which is saponified by the HCl formed in the previous reactions: $CCl_3.CH(OEt)_2 + HCl = CCl_3.CH(OH)(OEt) + EtCl$ (Lieben, *C. R.* 44, 1345; *B.* 3, 910). Wurtz (*C. R.* 74, 777) considers that chloro-ether is first formed, thus: $CH_3CHO + HOEt + HCl = H_2O + CH_3.CHCl(OEt)$, and this is then converted into tetra-chloro-ether $CCl_3.CHCl(OEt)$, which is converted by alcohol into tri-chloro-acetal $CCl_3CH(OEt)_2$, which is then decomposed by HCl as above.

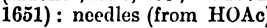
Estimation.—By shaking with standard NaOH and determining the amount of alkali neutralised.

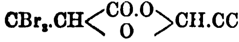
Properties.—A liquid with odour resembling aldehyde. It solidifies when shaken with a little water, forming so-called chloral hydrate, but it dissolves in much water. It reduces ammoniacal silver nitrate with formation of a mirror. It is not affected by distillation over quicklime or BaO as long as the oxide is covered by the liquid. It combines with NH_3. When introduced into the blood it is split up into chloroform and formic acid (Liebreich; Personne, *C. R.* 69, 979; Byasson, *C. R.* 72, 742; Arloing, *C. R.* 89, 245, 626; *cf.* Thomaszewicz, *Pf.* 9, 35). Tanret supposed that its physiological action was due to the liberation of CO in the blood (*J. Ph.* [4] 20, 355). Some of the chloral passes into the urine as urochloralic acid $C_8H_{11}Cl_3O_7$.

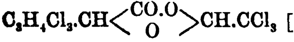
Reactions.—1. Split up at once by NaOH into chloroform and sodium formate, thus:

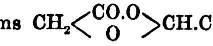
$$CCl_3.CHO + NaOH = CCl_3H + NaCHO_2.$$

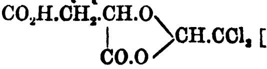
Alcoholic KOH and NaOEt act similarly, forming formic ether and chloroform (Kekulé, *A.* 119, 187). 2. Zn and HCl *reduce* it to aldehyde (Personne, *A.* 157, 113; *C. R.* 71, 227). Zinc-dust and water reduce it, on heating, to CH_4, CH_2Cl_2, and CH_3Cl (Cotton, *Bl.* [2] 42, 622).—3. Fuming HNO_3 *oxidises* it to tri-chloro-acetic acid. CrO_3 or HgO gives CO and CO_2. $KMnO_4$ gives CO_2, chloroform, oxygen, and chlorine (Cotton, *Bl.* [2] 43, 420).—4. *Chlorine* in sunlight forms CCl_4, hydric chloride, and $COCl_2$ (Gautier, *Bl.* [2] 45, 86; *C. R.* 101, 1161).—5. *Bromine* forms $CCl_3CO.Br$, CCl_3Br, CO, and HBr (Oglialoro, *B.* 7, 1461).—6. PCl_5 forms $CCl_3.CCl_2H$ (Paterno, *G.* 1, 590; *Z.* [2] 5, 245).—7. PCl_3Br_2 forms CCl_3CBr_2H.—8. H_2SO_4 forms chloralide crystals (*q. v.*). Fuming H_2SO_4 forms a crystalline compound (*v. infra*).—9. KIAq forms iodine and chloroform. 10. Al_2Cl_6 forms parachloral (240°) and C_2Cl_4 (Combes, *A. Ch.* [6] 12, 298).—11. P_2S_5 forms C_2HCl_3 (88°) (Paterno a. Oglialoro, *G.* 3, 538). 12. *Aniline* reacts violently forming tri-chloro-ethylidene-di-phenyl-di-amine $CCl_3.CH(NHPh)_2$ [101°] (Wallach, *B.* 5, 251).—13. *Acetamide* combines forming $CCl_3.CH(OH)(NHAc)$ (*v.* CHLORAL-AMMONIA).—14. *Acetonitrile* forms $CCl_3CH(NHAc)_2$ (Hübner, *B.* 6, 109; *Z.* 1871, 712; Hepp, *B.* 10, 1651): needles (from HOAc).—15. Heated with syrupy *lactic acid* at 160° chloral forms tri-chloro-ethylidene mono-lactate:


$CH_3.CH<\substack{CO.O\\O}>CH.CCl_3$ [45°] (223°) (Wallach, *A.* 193, 36). This body may also be got by dissolving chloral hydrate (1 pt.) in syrupy lactic acid, and adding H_2SO_4 (1 pt.) (M. Nencki, *J. pr.* 125, 239). In a similar way, *tri-chloro-lactic acid* heated with chloral forms chloralide (*q. v.*); *tri-bromo-lactic acid* forms tri-chloro-ethylidene tri-bromo-lactate

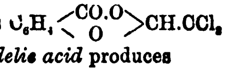

$CBr_3.CH<\substack{CO.O\\O}>CH.CCl_3$ [132°-135°]; *tri-chloro-α-oxy-valeric acid* forms

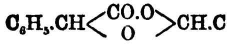

$C_3H_4Cl_3.CH<\substack{CO.O\\O}>CH.CCl_3$ [88°], (297°); glycollic acid forms


$CH_2<\substack{CO.O\\O}>CH.CCl_3$ [42°]; *malic acid* forms tri-chloro-ethylidene malate


$\begin{array}{l}CO_2H.CH_2.CH.O\\ \qquad\quad | \\ \qquad\quad CO.O\end{array}>CH.CCl_3$ [140°] (Wallach, *A.* 193, 37); *tartaric acid* gives

$CCl_3.CH<\substack{O\\O.CO}>CH.CH<\substack{O\\O.CO}>CH.CCl_3$; *salicylic acid* forms


$C_6H_4<\substack{CO.O\\O}>CH.CCl_3$ [124°]; while *mandelic acid* produces


$C_6H_5.CH<\substack{CO.O\\O}>CH.CCl_3$ [82°].—16. When mixed with *benzene* (1 mol.) and concentrated sulphuric acid, di-phenyl-tri-chloro-ethane $CCl_3.CH(C_6H_5)_2$ is formed (Goldschmiedt, *B.* 6, 985). Bromo- and chloro-benzene and toluene act similarly (Zeidler, *B.* 7, 1180; Fischer, *B.* 7, 1191).—17. By acting on *benzene* with chloral in the presence of aluminium chloride a liquid is obtained having the formula $C_6H_5.CCl_2.COH,HCl$ which by oxidation forms the acid $C_6H_5.CCl_2.COOH$ (Combes, *C. R.* 98, 678; *Bl.* [2] 41, 382).—18. *Zinc methide* (1 mol.) followed by water forms $CCl_3.CH(OH).CH_3$. Excess of $ZnMe_2$ followed by water forms $(CH_3)_2CH.CMe_2.OH$.—19. *Zinc ethide* followed by water forms tri-chloro-ethyl alcohol $CCl_3.CH_2.OH$.—20. *Hydroxylamine* forms chloro-glyoxim $C_2H_3ClN_2O_2$.

Combinations.—1. With *water* v. *Chloral hydrate.*

2. With *alcohols* v. *Chloral hydrate.*

3. With *hydric sulphide*: $(C_2Cl_3HO)_2H_2S$. [128°]. Formed by passing H_2S into a solution of chloral (Hagemann, *B.* 5, 154; Wyss, *B.* 7, 211; Paterno a. Oglialoro, *G.* 3, 533). Rhombohedra (from chloroform). Insol. water, sol. alcohol and ether. Decomposed by heat. With PCl_5 it gives $CCl_3.CHCl_2$. Gives with AcCl a di-acetyl derivative [78°].

4. With *phosphuretted hydrogen*: $(CCl_3CHO)_2PH_3$. [143°]. From chloral (3 g.) and PH_4I (2 g.). Small prisms (from ether). Decomposed by conc. NaOH into formate, hypophosphite, and hydrogen (Girard, *A. Ch.* [6] 2, 43).

5. With *mercaptan*: $C_2Cl_3HO,HSEt$. Crystalline.

6. With *acetyl chloride*: $CCl_3CHCl(OAc)$. (c. 187°). S.G. $\frac{17}{}$ 1·476 (V. Meyer, *B.* 3, 445; *A.* 171, 67; *cf.* Curie a. Millet, *C. R.* 83, 745).

7. With *acetic anhydride*: $CCl_3CH(OAc)_2$. (222°). S.G. $\frac{11}{}$ 1·422. Oil

8. With *ethylamine*: $CCl_3.CH(OH)NHEt$. On distillation this forms $CHCl_3$ and ethyl-formamide H.CO.NHEt.

9. With *fuming sulphuric acid*: $(C_2Cl_3HO)_5,SO_3,2H_2SO_4$. [70°]. Chloral (1 pt.) is mixed with fuming sulphuric acid (5 pts.). The product is washed with cold water and crystallised from ether (Grabowski, *B.* 6, 225, 1070). A mixture of chloral with an equal volume of fuming sulphuric acid forms large crystals of $(CCl_3.CHO)_4,H_2S_2O_7$.

10. With *alkaline bisulphites*: $C_2Cl_3HO,KHSO_3$ (Städeler, *A.* 106, 253; Rathke, *A.* 161, 154). This compound is also formed when K_2SO_3 is used, but if the solution be heated to 80° $(SO_3K)_2CH.CHO,KHSO_3$ aq crystallises out, while the mother-liquor contains $C_6H_{22}Cl_9S_7O_{31}K_7$.

11. With *hydrogen cyanide*: $CCl_3CH(OH)CN$. *Tri-chloro-lacto-nitrile.* [61°]. (c. 218°). Prepared by the action of anhydrous *prussic acid* at 120° upon chloral (Hagemann, *B.* 5, 151) or by boiling chloral with strong prussic acid (Bischoff a. Pinner, *B.* 5, 113; *A.* 179, 77). Trimetric plates (from CS_2). Saponified by HCl forming tri-chloro-lactic acid. Saponified by KOH forming potassic formate and cyanide and chloroform. With urea it forms $CCl_3CH(NH.CO.NH_2)_2$ (Pinner, *B.* 20, 2345). **Acetyl derivative.**—$CCl_3CH(OAc)CN$. [31°]. (208°). From acetic anhydride and the above (Pinner a. Fuchs,

B. 10, 1059). Rhombohedra. Insol. water, sol. alcohol. Conc. H_2SO_4 in the cold forms $CCl_3.CH(OAc).CO.NH_2$.

12. Another compound with *hydrogen cyanide*: $(CCl_3.CHO)_3.CNH$. [123°]. From conc. solutions of chloral and of KCN (Cech, *B.* 9, 1020). Prisms (from ether or benzene). Insol. water. Alcoholic potash (or even alcohol alone) forms di-chloro-acetic ether. On distillation it splits up into chloral and chloralide (Wallach, *B.* 6, 114). Alcoholic, or dilute aqueous, solutions of KCN convert chloral into di-chloro-acetic acid (or ether).

13. With *cyanic acid*: $(C_2Cl_3HO)_2CNOH$ [c. 169°]. Formed by passing vapour of cyanic acid into chloral, boiling the product with HCl and crystallising the residue from ether. Small prisms (Bischoff, *B.* 5, 86).

14. With both *cyanic* and *prussic acids*, C_2Cl_3HO, CNH, CNOH. [80°]. Prepared by pouring a solution of CNOK upon a mixture of solutions of chloral and KCy. Needles. Decomposed by hot water. Converted by ethylamine into $CCl_2(NEtH)CHO$. [45°] (Cech, *B.* 8, 1174; 9, 1253; 10, 880).

15. With *sodium acetate*: $CCl_3CH(OAc)(ONa)$. Minute white crystals, decomposed by water and alcohol (Rebuffat, *G.* 17, 406).

16. With *carbamic ether*: $CCl_3.CH(OH).NH.CO_2Et$. [103°]. Flaky mass (from ether-alcohol), formed by adding conc. HCl to a solution of carbamic ether in chloral (Bischoff, *B.* 7, 631). Resolved into its components by hot water or by heating at 100°.

17. With *urea*: $CCl_3.CH(OH).NH.CO.NH_2$. [150°]. From chloral and a conc. aqueous solution of urea. Scales. Decomposed on melting into chloral and cyanuric acid. The compound $(CCl_3.CH(OH).NH)_2CO$ [190°] is also formed, and differs from the preceding in being nearly insol. boiling water (Jacobsen, *A.* 157, 246).

18. With *benzamidoxim*: $C_9H_9N_2Cl_3O_2$. [135°]. White powder, insol. water, v. sol. alcohol and ether. Resolved by boiling dilute H_2SO_4 into its constituents (Falck, *B.* 19, 1481).

19. With *hexamidoxim*: $C_8H_{15}N_2Cl_3O_2$. [130°]. White pearly plates. Formed by heating the components together for a long time (Jacoby, *B.* 19, 1505).

20. With *thio-benzamide*: $CCl_3.CH(OH).NH.CS.C_6H_5$. [104°]. From chloral and thio-benzamide (Spica, *G.* 16, 182). Rhomboidal prisms of alliaceous odour, sl. sol. water, sol. alcohol and ether.

Chloral-ammonia $CCl_3.CH(OH).NH_2$. [64°].

Formed by passing NH_3 into a solution of chloral in chloroform (Städeler, *A.* 106, 253; Schiff, *B.* 10, 167). Insol. cold water, decomposed by hot water into $CHCl_3$ and ammonic formate (Personne, *A* 157 114). Boiling alcoholic KCN converts it into di-chloro-acetamide (R. Schiff a. Speciale, *G.* 9, 338). With benzoic aldehyde it gives $CCl_3.CH(OH).N:CHPh$ [130°], which crystallises from benzene in white leaflets, resolved by dilute acids into benzoic aldehyde, chloral, and NH_3 (Schiff, *G.* 9, 436).

Acetyl derivative.—$CCl_3CH(OH)NHAc$. *Chloral-acetamide.* [156°]. Formed by the action of acetyl chloride or acetic anhydride on the above; or from chloral and acetamide. Trimetric plates (from water). Insol. ether. Decomposed by heat into chloral and acetamide. Alcoholic KCN forms $C_{11}H_{18}Cl_8N_4O_5$. [120°] (S. a. S.).

Di-acetyl derivative. $CCl_3.CH(OAc)(NHAc)$. [118°]. Formed by the action of ClAc at 120° on the preceding. Decomposed by warm water into the preceding and acetic acid, the group (OAc) being unstable in presence of so much chlorine.

Dichloracetyl derivative. $CCl_3.CH(OH).NH.CO.CHCl_2$. [105°]. From chloral and di-chloro-acetamide (S. a. S.). Large prisms (from water).

Benzoyl derivative. $CCl_3.CH(OH).NHBz$. [151°]. From benzamide and chloral (Jacobsen, *A.* 157, 245) or by passing HCl into a mixture of chloral-hydrate and benzonitrile (Pinner a. Klein, *B.* 11, 10). Tables (from alcohol). Alcoholic KCN forms a compound $C_{20}H_{14}Cl_4N_4O$ [131°], which separates in small crystals from ether (S. a. S.).

Chloral hydrate $C_2H_3Cl_3O_2$ *i.e.* $CCl_3.CH(OH)_2$. *Tri-chloro-acetic ortho-aldehyde.* Mol. w. 165·5. [57°]. (97°). S.G. $\frac{50}{50}$ 1·6415 (Perkin, *C. J.* 51, 808); $\frac{60}{4}$ 1·575; S.G. (solid) 1·901. V.D. 2·8 (corresponding to a mixture of water and chloral). S. (in CS_2) 2 at 15°; 20 at 46°. R_∞ 47·94 (in a 33·2 p.c. aqueous solution) (Kanonnikoff, *J. pr.* [2] 31, 347). M.M. (fused) 7·151 at 54·6°; (in aqueous solution) 7·02 at 14°.

Formation.—By direct union of chloral with water, absorption of heat taking place (Phipson, *C. N.* 25, 257).

Preparation.—Alcohol (400g. of 97 per cent.) is poured upon crystallised ferric chloride (5g. of Fe_2Cl_6 12aq) and a large excess of chlorine is passed in. The product is distilled. The distillate contains chloral and chloral hydrate but not chloral alcoholate. After rectification the portion boiling between 94° and 97° is converted by water into chloral hydrate (525 g.) (Page, *A.* 225, 220; *cf.* Detsenyl, *C. C.* 1873, 767). Chloral hydrate may also be purified by crystallisation from CS_2 (Fluckiger, *Z.* 6, 432).

Properties.—Monoclinic plates, v. sol. water and alcohol. By shaking with conc. H_2SO_4 it is at once converted into chloral. In doses of more than 5 g. it produces sleep (Liebreich, *B.* 2, 269). It is antiseptic, preventing putrefaction of proteids. The vapour of chloral hydrate is split up by heat into chloral and water; the dissociation is complete at 100° at the ordinary pressure, and even at 61° under a pressure of 9 mm. (Wurtz, *C. R.* 89, 190; *cf.* Moitessier a. Engel, *C. R.* 86, 971; Troost, *C. R.* 84, 708; 85, 32, 400; 100, 834; *A. Ch.* [5] 13, 411; 22, 155; Friedel, *Bl.* [2] 43, 56; *C. R.* 100, 891; Naumann, *B.* 9, 822).

The molecular magnetic rotation indicates that chloral hydrate exists as such in its aqueous solution. In amyl oxide solution it begins to dissociate between 30° and 40° (Perkin, *C. J.* 51, 808). Chloral hydrate differs from chloral in not exhibiting Schiff's test for aldehydes with rosaniline and SO_2 (V. Meyer a. Caro, *B.* 13, 2343).

Detection.—Chloral hydrate may be extracted by ether from its aqueous solution (*e.g.* urine) and the following tests may then be applied: (*a*) Warming with alcoholic KOH and aniline gives (even with ·000015g.) the disgusting odour of phenyl carbamine. (*b*) Warming at 50° with conc. KOHAq and a little phenol gives a blue colour (with ·00005g.). (*c*) After boiling with potash formic acid may be detected (with ·00011g.). (*d*) Lime-water and H_2S give a pink colour (with ·00066g.) (Dragendorff a. Tiesenhausen, *C. C.* 1886, 636). The valuation of chloral hydrate may be effected by decomposing it with ammonia, KOHAq, or, better, with H_2SO_4 (Versmann, *Ph.* [3] 1, 701, 965;, Wood, *Ph.* [3] 1, 703; *cf.* Müller, *Z.* [2] 7, 66; *C. J.* 24, 444; Paul, *Ph.* [3] 1, 621; *C. J.* 24, 134).

Reactions.—1. With KCy it forms di-chloro-acetic acid.—2. Heated with *glycerin* it forms chloroform, formic acid, and allyl formate (Byasson, *C. R.* 75, 1628).—3. Boiled with *ammonic acetate* it forms chloralimide, $CCl_3.CH{:}NH$ (Pinner a. Fuchs, *B.* 10, 1068).—4. Warmed with aqueous KHS deposits sulphur, and then crystals of $C_4H_7Cl_3O_2S$ [97°] (Michael, *B.* 9, 1267; *cf.* Nicol, *C. N.* 43, 43).—5. With aqueous *ammonic sulphide* it forms a red powder $C_{18}H_{24}S_{13}N_4O_6$. This dye separates from petroleum in lustrous green crystals (E. Davy, *P. M.* [4], 68, 247; Lerch, *C. C.* 1887, 299).—6. Melted with $KClO_3$ it reacts violently with production of tri-chloro-acetic acid and decomposition products (Seubert, *B.* 18, 3336).—7. Boiled with *zinc-dust* it is decomposed with formation of chloride and oxychloride of zinc and liberation of hydrogen and CH_4 (Cotton, *Bl.* [2] 42, 622).—8. HgO decomposes chloral hydrate with formation of $COCl_2$, carbonic oxide, and CO_2.—9. $KMnO_4$ liberates chlorine, CO_2, and oxygen with formation of $CHCl_3$ (Cotton, *Bl.* [2], 43, 420).—10. Heated with ammonic sulphocyanide forms a white crystalline body $C_5H_5Cl_6N_3S$, insol. water, sol. alcohol (Nencki a. Schaffer, *J. pr.* 126, 430; Brodsky, *M.* 8, 27).—11. *Camphor* forms an unstable compound (vol. i. 670).—12. *Acetyl chloride* forms $CCl_3.CHCl(OAc)$ (Meyer a. Dulk, *B.* 4, 963).—13. With *di-methyl-aniline* and $ZnCl_2$ it gives $CCl_3.CH(OH).C_6H_4NMe_2$ (Knoeffler a. Boessneck, *B.* 20, 3193).

Acetyl derivative $CCl_3.CH(OAc)_2$. (222° uncor.). S.G. ^{11} 1·422. From chloral and Ac_2O. Liquid, insol. water, not attacked by cold KOHAq (Geuther, *A.* 106, 249).

Ethyl ether $CCl_3.CH(OH)(OEt)$.

Chloral alcoholate. Mol. w. 193·5. [56°]. (Jacobsen); [46°] (Lieben, *B.* 3, 909). (115°) (Martius a. Bartholdy, *B.* 3, 443). S.G. $\frac{66}{4}$ 1·329. V.D. (air = 1): 3·49 at 200° (theory: 6·68). The vapour-pressure has been examined by Ramsay a. Young (*C. J.* 49, 686). Formed by the union of chloral with alcohol (Personne, *C. R.* 69, 1363; *cf.* Roussin, *C. R.* 69, 1144; Thomsen, *B.* 2, 597; Lieben, *B.* 3, 907; Jungfleisch, Lebaigne a. Roucher, *J. Ph.* [4] 9, 208). Its vapour is dissociated by heat. Separated from aqueous solution by $CaCl_2$. Decomposed by H_2SO_4 with liberation of chloral. With PCl_5 it gives tetra-chloro-ether, $CCl_3.CHCl.OEt$ (Henry, *C. J.* 24, 255, 696; *B.* 4, 101, 435).

Ethyl-acetyl derivative $CCl_3(OAc)(OEt)$. (198° uncor.). S.G. ^{11} 1·327. From chloral alcoholate and AcCl. Also from tetra-chloro-ether and AgOAc (Busch, *B.* 11, 447).

Methyl-ethyl ether $CCl_3(OMe)(OEt)$. (193·4°). S.G. ^{24} 1·32. From tetra-chloro-ether and MeOH (Magnanimi, *G.* 16, 330). Liquid smelling like camphor.

Chloro-ethyl ether $CCl_3.CH(OH)OCH_2.CH_2Cl$. From chloral and glycolic chlorhydrin. Converted by PCl_5 into $CCl_3.CHCl.O.CH_2.CH_2Cl$ (Henry, *B.* 7, 763).

Methyl ether $CCl_3.CH(OH)(OMe)$. *Chloral methyl-alcoholate.* [50°]. (106°) (Jacobsen, *A.* 157, 243); (98°) (Bartholdy a. Martius, *B.* 3, 443). From chloral and methyl alcohol.

Di-methyl ether $CCl_3.CH(OMe)_2$. (183°). S.G. 1·28. From $CCl_3.CHCl.O.CH_3$ and MeOH. Liquid, smelling of camphor (Magnanimi, *G.* 16, 330).

Di-ethyl ether $CCl_3.CH(OEt)_2$. *Tri-chloro-acetal.* (197°) (B.); (200°) (W. a. V.); (205° cor.) (P. a. P.). S.G. 2·281 (P. a. P.). S. ·5. Formed by passing chlorine into dilute (75 p.c.) alcohol; or by treating chloral alcoholate with chlorine at 80° (Byasson, *Bl.* [2] 32, 304; *C. R.* 87, 26). Formed also by treating tetra-chloro-ethyl oxide $CCl_3.CHCl.OEt$ with alcohol in sealed tubes (Wurtz a. Vogt, *C. R.* 74, 777; Paterno a. Pisati, *G.* 2, 333). Liquid, smelling like di-chloro-acetal. Miscible with alcohol and ether. By heating with water or H_2SO_4 it is resolved into chloral and alcohol. Hot alkali has no action. HNO_3 gives tri-chloro-acetic acid. A solid isomeride is described under **CHLORO-ACETIC ALDEHYDE.**

Allyl ether $CCl_3.CH(OH)(OC_3H_5)$. *Chloral allyl-alcoholate.* [21°]. (116°). From chloral and allyl alcohol. Needles (Oglialoro, *B.* 7, 1462).

Acetyl derivative $CCl_3.CH(OAc)(OC_3H_5)$. (106°) (Oliveri, *G.* 14, 13).

Isoamyl ether $CCl_3.CH(OH)(OC_5H_{11})$. *Chloral amyl-alcoholate.* [56°]. (146°). S.G. (liquid) ^{25} 1·234.

Cetyl ether $CCl_3.CH(OH)(C_{16}H_{33})$. *Chloral cetyl-alcoholate.* Very small needles.

Ethylene ether $CCl_3.CH(OH).OC_2H_4O.CH(OH).CCl_3$. *Chloral glycolate.* From chloral and glycol (Henry, *B.* 7, 762).

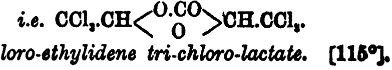
Isomeride of chloral hydrate. Chloral mixed with glacial HOAc and evaporated quickly is converted into an isomeride of chloral hydrate [80°], although the same solution when evaporated slowly deposits ordinary chloral hydrate [57°] (V. Meyer, *B.* 6, 449; *A.* 171, 74).

Meta-chloral $(C_2Cl_3HO)_n$. Formed by leaving chloral to stand with H_2SO_4. Chloral that has been freed from all traces of H_2SO_4 by distillation over BaO remains liquid for years (Byasson, *C. R.* 91, 1071). Amorphous solid, insol. water. HNO_3 oxidises it to tri-chloro-acetic acid. Alkalis form formate and chloroform. At 180° it is converted into ordinary chloral (Kolbe, *A.* 54, 183). Trimethylamine also polymerises chloral.

Parachloral $(C_2Cl_3HO)_n$. (240°). Formed, together with tetra-chloro-ethylene, by treating chloral with Al_2Cl_6 (Combes, *A. Ch.* [6] 12, 268). Liquid; oxidised by HNO_3 to tri-chloro-acetic acid.

'Para-chloralide' $(C_2Cl_3HO)_n$. (182°). S.G. ^{14} 1·577. An isomeride of chloral said to be formed by the action of chlorine on methyl alcohol (Cloez, *A.* 111, 178).

CHLORALIDE $C_5H_2Cl_6O_3$



$$\text{i.e. } CCl_3.CH\Big\langle\begin{matrix}O.CO\\O\end{matrix}\Big\rangle CH.CCl_3.$$

Tri-chloro-ethylidene tri-chloro-lactate. [115°].

(273°). V.D. 11·3 at 300° (calc. 11·2). Formed, together with meta-chloral, by the action of H_2SO_4 on chloral. Also by heating chloral with tri-chloro lactic acid at 150° (Wallach, *A.* 193, 1; *B.* 8, 1578).

Preparation.—Chloral hydrate (1 vol.) is heated at 90° with a mixture of conc. H_2SO_4 (1½ vols.) and fuming H_2SO_4 (1½ vols. of S.G. 1·85) in a flask with inverted condenser until crystallisation begins in the neck of the flask. The contents are shaken till cold, and then poured into water. The insoluble chloralide is washed with water and recrystallised from ether or chloroform (Otto, *A.* 239, 262; *cf.* Städeler, *A.* 61, 104; Grabowsky, *B.* 8, 1433; Kekulé, *A.* 105, 293).

Properties.—Monoclinic prisms (from ether). Insol. water, sl. sol. cold alcohol. Distils without decomposition. Boiling KOH splits it up into chloroform and formic acid. Alcohol at 150° gives chloral alcoholate and ethyl tri-chloro-lactate [67°]. Zn and HCl in alcoholic solution reduce it to aldehyde and di-chloro-acrylic acid. PCl_5 forms an oil $C_5HCl_7O_3$. S.G. $\frac{20^\circ}{4}$ 1·7436 (Anschutz a. Haslam, *A.* 239, 300).

CHLORANIL *v.* Tetra-chloro-quinone.

CHLOR-ANILIC ACID *v.* Di-chloro-di-oxy-quinone.

CHLORATES and **PERCHLORATES**—*Salts of chloric and perchloric acids, v.* Chlorine, oxy-acids of.

CHLORHYDRIC ACID. HCl (*Hydrochloric acid. Hydrogen chloride. Muriatic acid gas*). Mol. w. 36·37. [−112·5°] (solidifies at −115·7°) (Olszewski, *M.* 5, 127). V.D. 18·2. S.H.p. (13°–100°) (equal mass of water = 1) ·194 (Strecker, *W.* 17, 85); (27°–214°) ·1867 (Regnault, *Acad.* 26, 1). S.H.v. (equal mass of water = 1) ·1304; (equal volume of air = 1) ·975 (Clausius, *Mechan. Wärmetheorie*, 1, 62 [1876]. $\frac{\text{S.H.p.}}{\text{S.H.v.}}$ (20°) 1·389; (100°) 1·4 (Strecker, *W.* 19, 85; experimentally determined). C.E. (0°–33°) $V_t = V_0\,(1 + at + bt^2)$, values of *a* for $HCl + 6·5H_2O$ = ·000446; for $HCl + 50H_2O$ = ·000 0625; values of *b* for $HCl + 6·5H_2O$ = ·000 000 43; for $HCl + 50H_2O$ = ·000 008 71; for $HCl + 200H_2O$ = ·000 0153; for $HCl + 200H_2O$ = ·000 009 768 (Marignac, *A. Suppl.* 8, 335). S at 760 mm. (0°) 503; (4°) 490; (10°) 470; (20°) 440; (24°) 427; (36°) 396; (44°) 377; (48°) 367; (60°) 342. S. at 0° with varying pressure (60 mm.) 374; (100 mm.) 400; (200 mm.) 431; (300 mm.) 450; (400 mm.) 465; (600 mm.) 487; (800 mm.) 507; (1000 mm.) 522; (1300 mm.) 545 (Roscoe a. Dittmar, *A.* 112, 328; *v.* also Deicke, *P.* 119, 156). S. (alcohol, S.G. ·836) 327 (Pierre, *A. Ch.* [3] 31, 135). Vapour-pressure of liquid HCl (−73°) 1368 mm.; (−51°) 3800 mm.; (−30°) 8056 mm.; (0°) 19912 mm. (Faraday, *T.* 1845. 155). H.F. [H, Cl] = 22,000; [H, Cl, Aq] = 39,315 (*Th.* 2, 20). Critical point = 51·25° (Ansdell, *Pr.* 30, 117). S.G. liquid HCl (0°) ·908, (7·5°) ·873, (33°) ·748, (47·8°) ·619 (A.). Coefficient of compressibility (liquid HCl) for pressure from 52·8 to 208·19 atmos. at 47° = ·00166, at 33° = ·00096, at 15·85° = ·00062, at 5·7° = ·000397 (A.).

Occurrence.—In the gases of volcanoes, and in streams issuing in volcanic districts (Bunsen, *P.* 83, 197). In the gastric juice of mammals (Boedeker a. Troschel, *B. B.* 1854 486). An aqueous solution of HCl has been known for many centuries; the gas was first prepared approximately pure by Priestley in 1774. The acid was thought to be the oxide of an unknown element, *murium*, until Davy proved in 1810 that it was a compound of H and Cl.

Formation.—1. By the action of diffused sunlight on a mixture of equal volumes H and Cl. The mixture is best prepared by electrolysis of conc. HClAq, using carbon electrodes (Roscoe, *C. J.* 8, 16). Combination occurs explosively in direct sunlight, or in electric, or magnesium, light, or in the light produced by burning NO in CS_2 vapour. Combination may also be caused by heating to 150°, or by bringing the gases into contact with Pt black, or by absorbing them in charcoal. The gases do not combine in the dark at ordinary temperature. For details regarding the rate of combination by exposure to light *v.* Chemical change, vol. i. p. 749. 2. By the action of Cl on H_2O in sunlight; or Cl on H_2S, HI, turpentine, and many other organic compounds.—3. By the action of H_2SO_4Aq or other acid on various metallic chlorides.—4. By the action of superheated steam on $MgCl_2$, or on $CaCl_2$ mixed with sand.

Preparation.—1. By adding to 100 parts pure NaCl, in a flask with an exit tube and safety funnel, about 170 parts pure H_2SO_4Aq, prepared by diluting the conc. acid with ⅓ to ¼ its weight of H_2O and cooling, and gently warming. The gas is passed through a little conc. HClAq, and then dried by $CaCl_2$; it is collected over Hg, or by downward displacement of air. If the materials react in the proportions $NaCl:H_2SO_4$, $NaHSO_4$ and HCl are formed at ordinary temperatures; then adding NaCl and strongly heating, $NaHSO_4$ and NaCl give Na_2SO_4 and HCl. If HClAq is to be prepared, the gas is led into cold water, the exit tube passing only a little way under the surface: the HClAq may be purified by redistillation in contact with a little Cu (to remove Cl), after standing with pure $SnCl_2$ (to remove As), (*v.* Bettendorff, *Z.* [2] 5, 492; Zettnow, *D. P. J.* 205, 247; Hager, *Fr.* 1872. 306; Oster, *Fr.* 1872. 463; Houzeau, *A. Ch.* [4] 7, 484; Reinsch, *J. pr.* 24, 244; Otto, *B.* 19, 1903).—2. By dropping conc. H_2SO_4Aq, through a tube with glass stop-cock, into a flask about one-third filled with commercial HClAq; the liquid gets warm and all the HCl except about ·32 p.c. is evolved (P. Hoffmann, *B.* 1, 272). Liquid HCl may be prepared on a small scale by placing a few pieces of NH_4Cl in the closed end of a W shaped tube, running a little conc. H_2SO_4 by means of a bent funnel tube into the second bend of the tube, closing and thickening the open end, and, after cooling, allowing the acid to flow on to the NH_4Cl, and cooling the other limb of the tube. After a little the limb containing the reacting bodies is gently warmed when liquid HCl collects in the cooled limb (Davy a. Faraday, *T.* 1823. 164).

Properties.—HCl is a colourless gas with most irritating, acrid odour; it fumes in moist air. The dry gas does not redden litmus paper. At 10° under pressure of 40 atmospheres HCl condenses to a colourless liquid (Faraday, *T.* 1845, 155). HCl is largely absorbed by water with production of much heat; [HCl,Aq] =

17,314 (*Th.* 2, 19). The solution is strongly acid; the affinity is taken by Ostwald as 100 (*v.* Affinity, vol. i. p. 75). When heated, conc. HClAq gives off HCl and H_2O; the temperature rises to 110° at mean barometric pressure when a liquid S.G. 1·1 and containing 79·8 p.c. H_2O and 20·2 p.c. HCl distils over unchanged. This composition corresponds with the formula $HCl.8H_2O$; but it is not probable that the liquid is a definite hydrate; the B. P. and composition of the liquid vary with the pressure. The following numbers give the B. P. of HClAq, and the composition of the liquid remaining in the retort, at various pressures (Roscoe a. Dittmar, *A.* 112, 328; *v.* also Bineau, *A. Ch.* [3] 7, 257):—

Pressure in mm.	B.P.	P.c. HCl in residual liquid.
100	62°	22·8
200	76	22·1
300	84	21·7
490	97	20·9
760	110	20·2
1520	—	19·1
2280	—	18·1

If dry air is passed into conc. HClAq the liquid loses HCl; the residual liquid has a constant composition for a specified temperature. The following numbers give the composition of the HClAq remaining at *t*° after passage of dry air until HCl ceases to come off (Roscoe a. Dittmar, *A.* 112, 328):—

t°	P.c. HCl.	*t*°	P.c. HCl.	*t*°	P.c. HCl.
0°	25·0	35°	23·9	70°	22·6
5	24·9	40	23·8	75	22·3
10	24·7	45	23·6	80	22·0
15	24·6	50	23·4	85	21·7
20	24·4	55	23·2	90	21·4
25	24·3	60	23·0	95	21·1
30	24·1	65	22·8	100	20·7

The following table (Roscoe a. Dittmar) shows that the liquid obtained by passing air into HClAq at a specified temperature has, in many cases, the same composition as the liquid which boils at that temperature under a certain pressure:—

Pres. in MM.	B.P.	P.c. HCl.	Temp. with air-stream.	P.c. HCl.
100	61°-62	22·8	62°	22·9
210	76 -77	22·1	77	22·2
300	84 -85	21·7	85	21·7
380	91	21·3	91	21·4
490	97	20·9	98	21·1

The S.G. and composition of HClAq are given in the following table (Ure). Temp. 15°.

Acid of Sp. Gr. 1·2. p.ct.	Specific Gravity	Chlorine p.c.	HCl p.c.
100	1·2000	39·675	40·777
99	1·1982	39·278	40·369
98	1·1964	38·882	39·961
97	1·1946	38·485	39·554
96	1·1928	38·089	39·146
95	1·1910	37·692	38·738
94	1·1893	37·296	38·330
93	1·1875	36·900	37·923
92	1·1857	36·503	37·516
91	1·1846	36·107	37·108
90	1·1822	35·707	36·700
89	1·1802	35·310	36·292
88	1·1782	34·913	35·884
87	1·1762	34·517	35·476
86	1·1741	34·121	35·068
85	1·1721	33·724	34·660
84	1·1701	33·328	34·252
83	1·1681	32·931	33·845
82	1·1661	32·535	33·437
81	1·1641	32·136	33·029
80	1·1620	31·746	32·621
79	1·1599	31·343	32·213
78	1·1578	30·946	31·805
77	1·1557	30·550	31·398
76	1·1536	30·153	30·990
75	1·1515	29·757	30·582
74	1·1494	29·361	30·174
73	1·1473	28·964	29·767
72	1·1452	28·567	29·359
71	1·1431	28·171	28·951
70	1·1410	27·772	28·544
69	1·1389	27·376	28·136
68	1·1369	26·979	27·728
67	1·1349	26·583	27·321
66	1·1328	26·186	26·913
65	1·1308	25·789	26·505
64	1·1287	25·392	26·098
63	1·1267	24·996	25·690
62	1·1247	24·599	25·282
61	1·1226	24·202	24·874
60	1·1206	23·805	24·466
59	1·1185	23·408	24·058
58	1·1164	23·012	23·050
57	1·1143	22·615	23·242
56	1·1123	22·218	22·834
55	1·1102	21·822	22·426
54	1·1082	21·425	22·019
53	1·1061	21·028	21·611
52	1·1041	20·632	21·203
51	1·1020	20·235	20·796
50	1·1000	19·837	20·388
49	1·0980	19·440	19·980
48	1·0960	19·044	19·572
47	1·0939	18·647	19·165
46	1·0919	18·250	18·757
45	1·0899	17·854	18·359
44	1·0879	17·457	17·941
43	1·0859	17·060	17·534
42	1·0838	16·664	17·126
41	1·0818	16·267	16·718
40	1·0798	15·870	16·310
39	1·0778	15·474	15·902
38	1·0758	15·077	15·494
37	1·0738	14·680	15·087
36	1·0718	14·284	14·679
35	1·0697	13·887	14·271
34	1·0677	13·490	13·863
33	1·0657	13·094	13·456
32	1·0637	12·697	13·049
31	1·0617	12·300	12·641
30	1·0597	11·903	12·233
29	1·0577	11·506	11·825
28	1·0557	11·109	11·418
27	1·0537	10·712	11·010
26	1·0517	10·315	10·602
25	1·0497	9·919	10·194
24	1·0477	9·522	9·786
23	1·0457	9·125	9·372

Acid of Sp. Gr. 1·2. p. ct.	Specific Gravity	Chlorine p.c.	HCl p.c.
22	1·0437	8·729	9·971
21	1·0417	8·332	8·563
20	1·0397	7·935	8·155
19	1·0377	7·538	7·747
18	1·0357	7·141	7·340
17	1·0337	6·745	7·932
16	1·0318	6·348	6·524
15	1·0298	5·951	6·116
14	1·0279	5·554	6·709
13	1·0259	5·158	5·301
12	1·0239	4·762	5·893
11	1·0220	4·365	4·486
10	1·0200	3·968	4·078
9	1·0180	3·571	4·670
8	1·0160	3·174	3·262
7	1·0140	2·778	3·854
6	1·0120	2·381	3·447
5	1·0100	1·984	2·039
4	1·0080	1·588	2·631
3	1·0060	1·191	1·224
2	1·0040	0·795	1·816
1	1·0020	0·397	1·408

Kolb (*D. P. J.* 204, 322) gives the following table:—

S.G.	P.c. HCl at 0°.	100 parts acid at 15° contain			
		HCl	Acid of 20° Beaumé	Acid of 21° B.	Acid of 22° B.
1·000	0·0	0·1	0·3	0·3	0·3
1·007	1·4	1·5	4·7	4·4	4·2
1·014	2·7	2·9	9·0	8·6	8·1
1·022	4·2	4·5	14·1	13·3	12·6
1·029	5·5	5·8	18·1	17·1	16·2
1·036	6·9	7·3	22·8	21·5	20·4
1·044	8·4	8·9	27·8	26·2	24·9
1·052	9·9	10·4	32·6	30·7	29·1
1·060	11·4	12·0	37·6	35·4	33·6
1·067	12·7	13·4	41·9	39·5	37·5
1·075	14·2	15·0	46·9	44·2	42·0
1·083	15·7	16·5	51·6	48·7	46·2
1·091	17·2	18·1	56·7	53·4	50·7
1·100	18·9	19·9	62·3	58·7	55·7
1·108	20·4	21·5	67·3	63·4	60·2
1·116	21·9	23·1	72·3	68·1	64·7
1·125	23·6	24·8	77·6	73·2	69·4
1·134	25·2	26·6	83·3	78·5	74·5
1·143	27·0	28·4	88·9	83·8	79·5
1·152	28·7	30·2	94·5	89·0	84·6
1·157	29·7	31·2	97·7	92·0	87·4
1·161	30·4	32·0	100·0	94·4	89·6
1·166	31·4	33·0	103·3	97·3	92·4
1·171	32·3	33·9	106·1	100·0	94·9
1·175	33·0	34·7	108·6	102·4	97·2
1·180	34·1	35·7	111·7	105·3	100·0
1·185	35·1	36·8	115·2	108·6	103·0
1·190	36·1	37·9	118·6	111·8	106·1
1·195	37·1	39·0	122·0	115·0	109·2
1·199	38·0	39·8	124·6	117·4	111·4
1·205	39·1	41·2	130·0	121·5	115·4
1·210	40·2	42·4	132·7	125·0	119·0
1·212	41·7	42·9	134·3	126·6	120·1

Kremers (*P.* 108, 115) gives a table by which the S.G. of HClAq can be found at a temperature other than 19·5° which temperature is taken as normal. (See table on next page.)

Thus, an acid containing 25·5 p.c. HCl has S.G. = 1·101 at the normal temp. (19·5°), at 40° the S.G. will be $\frac{1{\cdot}101}{1{\cdot}00877} = 1{\cdot}092$, at 100° the S.G. will be $\frac{1{\cdot}101}{1{\cdot}03867} = 1{\cdot}06$. Thomsen, using the numbers in Ure's table, gives the S.G. of HClAq at 15° as $S.G. = \frac{100}{100-p} - \left(\frac{100-1{\cdot}0765\,p}{100-{\cdot}726\,p}\right)^{\frac{3}{2}}$, where p = p.c. of HCl (*P. Jubelband*, 144).

Reactions.—1. Decomposed by *heat*, at about 1500°, into H and Cl, which combine again on cooling. If a silver tube kept cold by running water is placed inside a porcelain tube in a wind furnace, and HCl is passed through the latter tube, the free Cl combines with the Ag, and H remains (Deville, *C. R.* 60, 317).—2. Moist, but not dry, HCl is decomposed by *oxygen* in presence of *sunlight* (Richardson, *C. J.* 51, 801).—3. *Electric sparks* very slightly decompose HCl.—4. Many *metals* decompose HCl when heated in it, giving chlorides and H; *metallic oxides* form H_2O and Cl; many metallic peroxides also set free Cl.—5. HCl is *not combustible.*—6. Mixed with *air* and passed through a hot porcelain tube, or over hot pumice, H_2O and Cl are formed (*comp.* CHLORINE; *Formation*, No. 3).—7. By the action of *platinum black* on a mixture of 1 vol. HCl with ¼ vol. O water is formed (Henry, *T.* 1800. 188).—8. HCl is completely decomposed by *sodium amalgam* at the ordinary temperature. (This is applied as a lecture experiment for demonstrating the composition of HCl, by Hofmann; *v. Einleitung in die moderne Chemie* (5th ed.), 73).—9. An *aqueous solution* of HCl exposed to air and sunlight evolves a little Cl.—10. Conc. HClAq evolves only H and Cl on *electrolysis*; diluted with 9 vols. or more H_2O, O is also evolved. Riche (*C. R.* 46, 348) says that by electrolysis of HClAq, $HClO_4Aq$ is formed.—11. Conc. HClAq heated to 200° with *amorphous phosphorus* produces PH_3 and H_3PO_4Aq.—12. An *aqueous solution* of HCl is decomposed by many *metals* with formation of chlorides and evolution of H. Let this decomposition be expressed by the equation $R + 2HClAq = RCl_2Aq + H_2$; then considered thermally this is composed of the parts (1) $-[H^2, Cl^2, Aq]$, (2) $+[R, Cl^2, Aq]$. The value of (1) is about 79,000, but is less the less the quantity of water used; for very conc. solutions it is equal to about 69,000: if then the value of $[R, Cl^2, Aq]$ is greater than 79,000 we should expect the metal R to decompose dilute HClAq; if $[R, Cl^2, Aq]$ is greater than 69,000 we should expect R to decompose conc. HClAq. $[R, Cl^2, Aq]$ is greater than 79,000 when $R = K_2$, or other alkali metal, Ag_2, Ca, Ba, Sr, Mg, Cd, Zn, Mn, Fe, Co, Ni, Sn. $[R, Cl^2, Aq]$ is less than 79,000 when $R = Tl_2$, Pb, Cu, Hg, Pd, Pt, or ⅓ Au_2; these metals do not decompose dilute HClAq. Now $[Pb, Cl^2, Aq] = 75,970$, which is > 69,000; Pb decomposes conc. HClAq. The following quantities of heat are produced, per 2 grams of H formed, by the action of certain metals on HClAq; these numbers afford approximate values of the relative intensities of the actions: Mg = 108,300;

HCl itself should always be called hydrogen chloride. M. M. P. M.

CHLORIDE OF LIME—*Bleaching powder*, *v.* HYPOCHLORITES under CHLORINE, OXY-ACIDS OF (p. 17).

CHLORIDES, ORGANIC *v.* CHLORO- COMPOUNDS.

CHLORINE. Cl. (*Dephlogisticated muriatic acid gas.*) At. w. 35·37. Mol. w. 70·74. (−33·6° at 760 mm.) (Regnault). Solidifies at about −102° (Olszewski, *M.* 5, 127). S.G. (liquid) 1·33 (Faraday, *T.* 1823, 160 a. 198). V.D. 35·8 (*v. Properties*, p. 11). S.H.p. (13°−202°) (equal mass of H_2O = 1) ·1241 (Regnault, *Acad.* 26, 1). S.H.v. (equal mass of H_2O = 1) ·0928; (equal volume of air = 1) 1·35 (Clausius, *Mechan. Warmetheorie*, [1876] 1, 62). $\frac{\text{S.H.p.}}{\text{S.H.v.}}$ (20°−34°) 1·323 (Strecker, *W.* 13, 20; experimentally determined). Vol. absorbed by 1 vol. H_2O at 760 mm. $= 3·0361 - ·046196t + ·0001107t^2$ (Schonfield, *A.* 95, 1). $\frac{A-1}{d} \times$ At. w. = 10·6 (Gladstone, *T.* 1870. 9). Emission-spectrum; principal lines are a group of 4 about 6670, followed by 9 others and then by one with wave-length 4130 (Salet, *A. Ch.* [4] 28, 24). Absorption-spectrum marked by many irregularly distributed lines; the violet is nearly wholly absorbed (Morren, *C. R.* 68, 376; Gernez, *C. R.* 74, 660).

Chlorine was discovered by Scheele in 1774 and supposed by him to be hydrochloric acid deprived of phlogiston. Berthollet regarded it as oxygenated hydrochloric acid; chlorine and hydrochloric acid were long supposed to be oxygen compounds of an unknown element. In 1809 Gay-Lussac and Thénard, showed that chlorine behaves like an element; in 1810 Davy established the elementary character of the body and gave it the name chlorine (χλωρός = yellow-green) (Scheele, *Opusc.* 1, 247; Berthollet, *Acad.* 1785. 286; Davy, *T.* 1810; Gay-Lussac a. Thénard, *G. A.* 35, 8; *A. Ch.* 91, 96).

Occurrence.—Never free; but in combination with very many metals in various rocks; in sea-water as NaCl; chlorides occur in plant-ash and in many parts of animals.

Formation. — 1. By the action of conc. HClAq on MnO_2 ($MnO_2 + 4HClAq = MnCl_2Aq + 2H_2O + Cl_2$); or better by using 1 part MnO_2, 2 parts HClAq (S.G. 1·14), and 1 part conc. H_2SO_4 diluted with its own weight of water ($MnO_2 + 2HClAq + H_2SO_4 = MnSO_4Aq + 2H_2O + Cl_2$). — 2. By the action of conc. H_2SO_4 on a mixture of NaCl and $NaNO_3$; the NO_2 produced is absorbed by conc. H_2SO_4 ($2NaCl + 2NaNO_3 + 2H_2SO_4 = 2Na_2SO_4 + 2NO_2 + 2H_2O + Cl_2$) (Dunlop, *D. P. J.* 151, 48).—3. By the action of a porous substance, *e.g.* clay, on HCl mixed with air. Deacon (*C. N.* 22, 157) soaks clay-bricks in saturated $CuSO_4Aq$, and heats them to 370°−400° in a stream of 5 vols. air and 4 vols. HCl; Cl is evolved (*v.* Deacon, *C. J.* [2] 10, 275). Probably $CuCl_2$ is formed and decomposed to Cu_2Cl_2 and Cl, and the Cu_2Cl_2 is again decomposed by the air to CuO and Cl, the CuO being changed to $CuCl_2$ by the HCl (Hengsen, *B.* 9, 1674).

Preparation. — 1. 100 grams pyrolusite (MnO_2) free from carbonates are well mixed with 130 grams NaCl, and placed in a capacious flask; a cold mixture of 125 c.c. conc. H_2SO_4 (S.G. 1·85) with 105 c.c. water is added. Cl is evolved; after a time the flask is warmed in a water bath; about 80 grams of Cl are obtainable from the above quantities. The Cl carries over with it a little HCl, and sometimes $MnCl_2$; it is passed through $CuSO_4Aq$ ($CuCl_2Aq$ and H_2SO_4 are formed) and then through water. If dry Cl is required the gas must be passed through several tubes containing $CaCl_2$ and through one or two long tubes filled with pumice soaked in boiled H_2SO_4. The gas may be collected by downward displacement, or over warm water or saturated NaClAq.—2. Crystals of $K_2Cr_2O_7$ are acted on by conc. HClAq in a capacious flask, the acid being added little by little ($14HClAq + K_2Cr_2O_7 = Cr_2Cl_6Aq + 2KClAq + 7H_2O + 3Cl_2$).—3. Chloride of lime is decomposed by HClAq ($Ca(ClO)_2 + 4HClAq = CaCl_2Aq + 2H_2O + 2Cl_2$). Kammerer (*B.* 9, 1548) describes a lecture-apparatus for the convenient preparation of Cl, based on this reaction. Dry chloride of lime, intimately mixed with burnt gypsum, is slightly moistened so that it can be rolled with difficulty into balls between the fingers; the mixture is powdered in an iron mortar and then beaten into an iron frame 10–12 mm. in height; the frame is then covered with oilcloth and very strongly compressed; the compressed plate is cut into cubes, which are preserved in a stoppered bottle. When these cubes are used in a Kipp's apparatus with HClAq of S.G. 1·124 (free from H_2SO_4) diluted with its own volume of water, a steady stream of chlorine is obtained (Winkler, *B.* 20, 184).

Liquid Chlorine is prepared (Faraday, *T.* 1823. 160 & 198) by placing crystals of $Cl.5H_2O$, thoroughly pressed between folds of paper at 0°, in the closed end of a Λ tube, closing the other end, placing the $Cl.5H_2O$ in water at 35°, and the other limb of the tube in a mixture of snow and salt (*v.* also Biewend, *J. pr.* 15, 440). Mohr (*A.* 22, 162) places a mixture of dry $KHSO_4$, NaCl, and MnO_2 in the longer limb of a Λ tube, and above this a layer of $CaCl_2$; the shorter limb is closed, and placed in a mixture of snow and salt; the mixture in the longer limb is then heated, and, when liquid Cl has collected in the other limb, is again cooled to prevent re-absorption of the Cl. The operation must be conducted in the dark, else HCl and O are produced, and the tube is liable to be broken. Liquid Cl is solidified by surrounding with liquid C_2H_4 and lowering the pressure (Olszewski, *M.* 5, 127).

Properties.—A greenish-yellow gas, becoming darker in colour when heated; very irritating odour; liquefied at 15° under pressure of 4 atmospheres (Faraday, *T.* 1823. 160 & 198); at 0° under pressure of 6 atmospheres, and at 12·5° under $8\frac{1}{2}$ atmos. (Niemann). Liquid Cl is dark yellow; immiscible with water, S.G. 1·33; B.P. −33·6° at 760 mm.; non-conductor of electricity (Regnault). Very poisonous; even when mixed with much air it attacks the mucous membranes and causes irritation and even blood-spitting. When working with Cl, the nose and mouth should be protected by a charcoal respirator, or by a cloth dipped in alcohol. Absorbed by porous substances, *e.g.* charcoal, with production of heat (*v.* Melsens, *C. R.* 76, 92); not combustible in O, but burns in H producing HCl. Dissolves in water with production of heat, $[Cl^2,Aq] = 2600$ (*Th.* 2, 400). Schönfield gives these data (*A.* 93, 26; 95, 8):—

1 *vol. water absorbs x vols. Cl at* 760 *mm.*

t°	*x*	*t*°	*x*	*t*°	*x*
10	2·5852	21	2·1148	31	1·7104
11	2·5413	22	2·0734	32	1·6712
12	2·4977	23	2·0322	33	1·6322
13	2·4543	24	1·9912	34	1·5934
14	2·4111	25	1·9504	35	1·5550
15	2·3681	26	1·9099	36	1·5166
16	2·3253	27	1·8695	37	1·4785
17	2·2828	28	1·8295	38	1·4406
18	2·2405	29	1·7895	39	1·4029
19	2·1984	30	1·7499	40	1·3655
20	2·1565				

Solubility is greatest at 10°; chlorine-water is therefore best prepared by leading Cl into H_2O kept at about 10° and repeatedly shaking. Solution of Cl in H_2O has smell of gaseous Cl; it freezes at 0°, giving Cl hydrate and ice (*v. Combinations*, No. 3); loses all Cl on boiling (on loss of Cl from Cl-water at 100° in closed vessels, *v.* Pickering, *C. J.* 37, 139); decomposes quickly in direct sunlight into HCl and O. The presence of HCl in Cl-water is detected by shaking with Hg until the smell of Cl is removed, filtering, and testing filtrate with blue litmus and with $AgNO_3Aq$.

The atomic weight of Cl has been determined (1) by analyses, and determinations of V.D., of many gaseous compounds, *e.g.* ClH, ClTl, Cl_2Zn, Cl_3Bi, Cl_4C, Cl_5Ta, Cl_6W, &c.; (2) by comparison of chlorides, &c., with isomorphous bromides, iodides, &c.; (3) by conversion of Ag into AgCl by Berzelius (*P.* 8, 17); by conversion of $NaClO_3$ and $KClO_3$ into NaCl and KCl by Penny (*T.* 129, 25); by conversion of $KClO_3$ to KCl, and $KClO_4$ to KCl, by Marignac (*A.* 44, 18); by conversion of $KClO_3$ to KCl by heat, and by decomposition of $KClO_3$ by HCl, by Stas (*Rech.* 118); by heating Ag in Cl, by ppg. Ag solution by gaseous HCl, also by HClAq, also by NH_4ClAq, by Stas (*Rech.* 38, 42, 44); by reducing $AgClO_3$ by SO_2Aq by Stas (*Nouv. R.* 208).

The atom of Cl is monovalent in gaseous molecules. Cl acts as a very negative, acid-forming, element; it appears to be positive to O, and probably to F. Combines with all elements except F, directly with all except N, O, C, and F, with many elements combination occurs at ordinary temperatures with production of much heat (*v.* Chlorides). Replacement of H in carbon compounds by Cl is usually accompanied by production, or increase, of acidic character; *e.g.* relative affinity of $CH_2Cl.CO_2H$ is greater than that of $CH_3.CO_2H$ (*v.* Affinity, vol. i. p. 83). Heats of formation, in solution, of metallic chlorides are greater than those of corresponding bromides or iodides; bromides are wholly or partially decomposed, iodides are easily decomposed, by Cl. At least two oxides of Cl are known as gases; one oxy-acid, $HClO_4$, has been obtained in separate and definite form (*v.* Chlorides; Halogen elements; and Halogen elements, binary compounds of).

The S.G. of Cl gas at 200° was found by Ludwig to be 2·45 (air = 1) (*B.* 1, 232). Many determinations have been made by V. Meyer and his pupils, using Cl prepared before and also during the experiments; the general result is that the S.G. of Cl is very slightly, if at all, less at high temperatures, 1000°-1400°, than at a red heat (*v.* Langer a. Meyer, *B.* 15, 2769; also Crafts, *B.* 16, 457); but that the S.G. of Cl formed in the apparatus by heating $PtCl_2$ at 1200°, is 2·05 (air = 1) in place of 2·45 calculated for Cl_2 (*v.* V. Meyer, *B.* 13, 721). The determinations of Jahn (*B.* 15, 1242) show that Cl does not attain the S.G. calculated for Cl_2 until it is heated to about 240° above its B.P.; the differences between the observed and calculated numbers are however very small, much less than the differences in the case of Br (*q. v.*) (*v.* Halogen elements).

Reactions.—1. Cl dissolves in *water* with production of heat $[Cl^2,Aq] = 2{,}600$ (*Th.* 2, 400); the solution decomposes, rapidly in direct sunlight, with formation of HCl and O; according to Popper (*A.* 227, 161) $HClO_3$ is also formed. Chlorine water therefore acts as an oxidiser, *e.g.* in bleaching (Poussaint, *A.* 137, 114). The thermal value is, $2[H,Cl,Aq] - [H^2,O] = 10{,}270$ (Thomsen).—2. Cl decomposes *steam* rapidly when a mixture of the two is passed through a red-hot tube.—3. Aqueous solutions of *potash* (or *soda*) absorb Cl, yielding KCl and KClO in cold, and KCl and $KClO_3$ in hot, solution: $Ca(OH)_2$ absorbs Cl forming CaOCl.Cl.—4. Aqueous *ammonia* yields NH_4Cl and N; if Cl is in excess chloride of N is formed.—5. The more *basic metallic oxides* are decomposed by Cl, when dissolved or suspended in water, with formation of metallic chloride and peroxide, or metallic chloride and an oxygen compound of Cl (*v.* Chlorine, oxides of). Many metallic oxides when heated in Cl give chlorides and O; in some cases, *e.g.* Al_2O_3, B_2O_3, O is removed only when Cl is passed over a hot mixture of the oxide with carbon.—6. All *compounds of hydrogen*, except HF, are decomposed by Cl with formation of HCl; many at ordinary temperatures; *e.g.* H_3P,H_3As, H_2S, HI.—7. All *metallic bromides, iodides, and sulphides* are decomposed either at ordinary or higher temperatures.—8. *Carbon compounds containing hydrogen* are usually easily decomposed by Cl, with formation of HCl, and frequently with separation of C; turpentine *e.g.* burns in Cl with a deposit of soot. Some vegetable colours are bleached by Cl by direct removal of H; in most cases, however, the action requires the presence of H_2O and is due to the O evolved in contact with the colouring matter. (For the reactions of Cl with Ag salts *v.* Krutwig, *B.* 11, 304.)—9. An aqueous solution of *sodium thiosulphate* is decomposed by Cl; the chief reactions are (1)

$$Na_2S_2O_3Aq + 5H_2O + 8Cl$$
$$= Na_2SO_4Aq + 8HClAq + H_2SO_4Aq;$$

(2) $Na_2S_2O_3Aq + 2Cl + H_2O = Na_2SO_4Aq + 2HClAq + S$; (3) $2Na_2S_2O_3Aq + Cl_2 = Na_2S_4O_6Aq + 2NaClAq$. On dilution H_2S is evolved; probably, $2Na_2S_2O_3Aq = Na_2S_3O_6Aq + Na_2SAq$; and then $Na_2SAq + 2HClAq$ (formed as in (1)) $= 2NaClAq + H_2S$ (*v.* Lunge, *B.* 12, 404).—10. Many *salts* are decomposed by Cl with formation

of aqueous solutions of $HClO$: *e.g.*

$$Na_2CO_3Aq + H_2O + 2Cl_2 = 2NaClAq + 2HOClAq + CO_2;$$

$CaCO_3$ (suspended in H_2O) + $H_2O + 2Cl_2 = CaCl_2Aq + CO_2 + 2HOClAq$: (*v.* CHLORINE, OXY-ACIDS OF).—11. *Iodine* suspended in water is converted into HIO_3: $I_2Aq + 5Cl_2 + 6H_2O = 2HIO_3Aq + 10HClAq$.

Combinations.—1. Directly with all *elements* except O, N, C, and F; indirectly also with O, N, and C. In most cases much heat is produced (*v.* CHLORIDES). Dry Cl has no action on dry Na (Wanklyn, *C. N.* 20, 271); K, Na, and Sb, do not combine with liquid Cl at − 80°; P and As on the other hand combine readily (Donny a. Mareska, *A.* 56, 160). The combination of Cl and H takes place slowly in the dark, but very rapidly and explosively in direct sunlight, in electric light, in Mg light, or in the light produced by burning CS_2 in NO; [H, Cl] = 22,000 (Thomsen). For more details regarding the combination of Cl and H *v.* CHLORHYDRIC ACID, p. 5; also CHEMICAL CHANGE, vol. i. p. 749.—2. Cl condensed in charcoal combines, without the aid of heat or light, with *sulphur dioxide* to form SO_2Cl_2 (Melsens, *C. R.* 76, 92).—3. Cl combines with *water*: when a saturated aqueous solution is cooled to 0°, or when Cl is led into H_2O kept nearly at 0°, crystals of $Cl.5H_2O$ separate out (Faraday, *Q. J. S.* 15, 71). This hydrate is best prepared by passing Cl into a little water in a flask surrounded by ice, till the water is changed to a thick yellowish magma; and then pressing strongly between thick layers of paper kept at 0°. $Cl.5H_2O$ at −50° forms white trimetric octahedra, which may be sublimed (? with partial decomposition) in a closed vessel filled with Cl, the upper part being kept below 0°. $Cl.5H_2O$ decomposes at ordinary temperatures and pressures with evolution of Cl and formation of Cl water; in a closed tube it separates into Cl and H_2O at about 35°; on cooling to 15° or so the $Cl.5H_2O$ is re-formed (*v.* p. 10, *Liquid chlorine*) (compare Wöhler, *A.* 85, 374).

Detection and Estimation.—Chlorine decomposes KIAq giving KClAq and IAq, the I is detected by the blue colour it produces with starch paste. Soluble chlorides ppt. Ag as white AgCl from $AgNO_3Aq$. Solid chlorides when heated with $K_2Cr_2O_7$ and conc. H_2SO_4 produce gaseous CrO_2Cl_2 which is easily condensed to a reddish-brown liquid; bromides and iodides under similar conditions give Br and I respectively.

Chlorine in dilute aqueous solutions may be estimated volumetrically (1) by determining the mass of I (by means of standardised $Na_2S_2O_3Aq$) set free from KIAq by the Cl, or (2) by gently warming in a closed vessel with excess of $Na_2S_2O_3Aq$—whereby part of the $Na_2S_2O_3$ is changed to $NaHSO_4$—decomposing the remaining $Na_2S_2O_3$ by boiling with HClAq, and estimating the sulphate produced by the usual methods. Chlorides, in solution, may be estimated (1) by ppg. as AgCl, washing, drying, slightly fusing, and weighing; or (2) volumetrically by means of standardised $AgNO_3Aq$, in presence of a very little K_2CrO_4Aq; the $AgNO_3Aq$ is added until the whole of the chlorine is ppd. as AgCl, the completion of the reaction being determined by noticing the production of red Ag_2CrO_4: the chloride ought to be present in the liquid as alkali or alkaline-earth chloride; the liquid must be neutral to litmus. The reaction of chlorides with $K_2Cr_2O_7$ and conc. H_2SO_4 may also be applied to the estimation of Cl in presence of I and Br (*v.* Dechan, *C. J.* [2] 49, 682). M. M. P. M.

CHLORINE, BROMIDE OF: better called **Bromine chloride**; *v.* BROMINE.

CHLORINE, CYANIDES OF: better called **Cyanogen chlorides**; *v.* CYANOGEN.

CHLORINE, HYDRATE OF. $Cl.5H_2O$. Obtained by passing Cl into H_2O at 0°; *v.* CHLORINE; *Combinations*, No. 3.

CHLORINE, IODIDES OF: ICl and ICl_3: better called **Iodine chlorides**; *v.* IODINE.

CHLORINE, OXIDES OF. Chlorine and oxygen do not combine directly. Two oxides of Cl, Cl_2O and ClO_2, certainly exist; a third is usually described as Cl_2O_3, but it is probably a mixture of ClO_2 and Cl (*v.* CHLORINE TRIOXIDE). They are all unstable bodies, easily decomposing into their elements. Cl_2O is the anhydride of HClO, but this acid is known only in dilute aqueous solutions. The anhydride Cl_2O cannot be obtained from solutions of the acid; Cl_2O is prepared by the action of Cl on dry HgO. The supposed Cl_2O_3 is said to be obtained by reducing $HClO_3Aq$, generally by As_4O_6. ClO_2 is not an anhydride of a definite acid; it is obtained by the action of H_2SO_4Aq on $KClO_3$; on addition of H_2O, or KOHAq, it forms $HClO_2Aq$ and $HClO_3Aq$, or $KClO_2Aq$ and $KClO_3Aq$. The hypothetical anhydrides of $HClO_3$ and $HClO_4$, viz. Cl_2O_5 and Cl_2O_7, are unknown. The heat of formation of Cl_2O is negative; $[Cl^2,O] = -17,900$ (Thomsen). The heat of formation of the only known oxide of I, viz. I_2O_5, has a large positive value $[I^2,O^5] = 45,000$ (Thomsen).

Berthelot discovered $KClO_3$ in 1786; it was long known as *oxidised potassium chloride*. Other compounds containing Cl and O were prepared and examined by Chevenix (1802), Stadion and Davy (1815), and by Balard (1834). Millon in 1843 added much to the knowledge of the oxy-compounds of Cl. In more recent times Carius, Brandau, and Pebal have examined these compounds. The body called by Davy *euchlorine*, obtained by the action of HClAq on $KClO_3$, and supposed by him to be an oxide of Cl, has been proved to be a mixture of ClO_2 with Cl. Millon's compounds Cl_6O_{13} and Cl_8O_{17} have also been shown to be mixtures (H. Davy, *T.* 1815. 214; Gay-Lussac, *A. Ch.* 8, 408; Soubeiran, *A. Ch.* 48, 113; J. Davy, *N. Ed. P. J.* 17, 49; Millon, *A. Ch.* [3] 7, 298; Pebal, *A.* 177, 1).

I. CHLORINE MONOXIDE. Cl_2O. (*Hypochlorous anhydride.*) Mol. w. 86·7. (5° at 738 mm.) (Garzarolli-Thurnlackh, *A.* 230, 273). V.D. 43·5 at 10°. $[Cl^2,O] = -17,930$ (*Th.* 2, 399). S.G. 2·977 (air = 1). Absorption-spectrum shows bands in blue and violet (Gernez, *C. R.* 74, 803). S. (0°) about 200.

Preparation.—Precipitated HgO is heated to about 300° for some time, and cooled (Pelouze, *A.* 46, 195); it is placed in a long tube surrounded by water; well washed and thoroughly dried Cl is passed through the tube. The reaction is $HgO + 2Cl_2 = HgCl_2 + Cl_2O$; the Cl_2O is passed into dry flasks; as each is filled it is closed with a glass stopper which is then covered with paraffin. If liquid Cl_2O is required the tube containing HgO is connected with a Y tube, the upper part of which is cooled to at least −20°. Ladenburg (*B.* 17, 157) recommends cooling by alcohol, the temperature of which is reduced to −40° by a small ammonia-freezing machine—dry test tubes surrounded by ice and salt are placed under the Y tube, and a few drops of Cl_2O are collected in each tube. In this way the principal reactions of liquid Cl_2O may be demonstrated without danger (*v.* Ladenburg, *l.c.*). If crystalline HgO is used, no action occurs between it and Cl; if ordinary ppd. HgO is employed the action is too rapid, much heat is evolved, and no Cl_2O, but only O, is obtained.

Properties.—Reddish-yellow gas, with very irritating odour: condenses at about −20° to a blood-red liquid which boils at about −17° (Pelouze, *A. Ch.* [3] 7, 176). Both gas and liquid are very easily decomposed, sometimes with violent explosion, into Cl and O; pouring the liquid from one glass vessel to another, or contact with a scratch on the glass, may suffice to bring about an explosion. Rise of temperature, or the action of electric sparks, causes the gas to explode, with production of Cl and O (Balard, *A. Ch.* 57, 225; Gay-Lussac, *C. R.* 14, 927). The gas is said to decompose in sunlight without explosion into Cl and O, the volumes of these gases being as 2:1.

Reactions and Combinations.—1. Powdered *metals* form chlorides and oxides, or oxychlorides, frequently with explosion.—2. Many *metallic oxides* react with the gas to form chlorides and higher oxides; Ag_2O gives AgCl and O.—3. *Phosphorus*, *Sulphur*, and *Selenium*, form chlorides and oxides, with explosion.—4. *Hydrogen*, in sunlight, decomposes the gas explosively, producing HCl and H_2O.—5. Freshly heated *carbon*, cooled under Hg, detonates in Cl_2O; Cl, O, and a little CO_2 are formed.—6. *Hydrochloric acid gas* forms H_2O and Cl.—7. *Acetic anhydride*, $(C_2H_3O)_2O$, absorbs the gas forming the very unstable compound $C_2H_3O.OCl$ (Schutzenberger, *C. R.* 53, 538).—8. The liquid Cl_2O sinks in *water*, and then slowly dissolves forming HClOAq (*q. v.*). Water at 0° absorbs more than 200 times its volume of gaseous Cl_2O: the solution contains HClO.

Method of Analysis. The gas was slowly passed through a narrow glass tube with three bulbs blown on it, the part of the tube before the first bulb being heated; by this means the gas was decomposed, and the three bulbs were filled with the products of this decomposition, viz., Cl and O. The bulbs were sealed by the blowpipe, and each was then opened under KOHAq; the Cl was thus absorbed while the O remained. The volume of KOHAq was measured; the bulbs were filled with KOHAq and the total volume was determined. The result was that 2 vols. Cl were found in each bulb with 1 vol. O. The weights of Cl and O formed were calculated, and the weight of the volume of the undecomposed gas which the bulb would contain when full was calculated from the observed S.G. of the gas. It was thus found that 2 vols. of the gas are decomposed by heat into 2 vols. Cl and 1 vol. O. This calculation assumes that the gas entering the small bulb contains no free Cl or O (Regnault).

References.—Berthollet, *Statique Chimique*, 2, 183. Wagemann, *G. A.* 35, 115. Geiger, *R. P.* 15, 40. Grouvelle, *A. Ch.* 17, 37. Berzelius, *P.* 12, 529. Liebig, *P.* 15, 541. Soubeiran, *A. Ch.* 48, 113. Balard, *A. Ch.* 57, 225. Martens, *A. Ch.* 61, 193. Gay-Lussac, *C. R.* 14, 927. Pelouze, *A. Ch.* [3] 7, 176. Kolb, *A. Ch.* [4] 12, 266.

II. CHLORINE PEROXIDE. ClO_2. (*Chlorine dioxide* or *tetroxide.*) Mol. w. 67·29. V.D. 38·5, 34·5 at 10·7° and 718 mm. (Pebal a. Schacherl, *A.* 213, 113). S.G. 2·315 (air = 1).

Preparation. — 1. About 100 grams pure conc. H_2SO_4 is placed in a platinum dish surrounded by snow and salt; from 15 to 20 grams dry finely powdered $KClO_3$ is added little by little, with stirring with a glass rod after each addition. When so much $KClO_3$ has been added that the contents of the dish form a thick oily liquid, this is carefully poured through a funnel into a glass flask, with the neck drawn out, of a size such that it is not more than one-third filled with the liquid. The greatest care must be taken to keep the neck of the flask perfectly free from the oily liquid. The flask is kept cold; a piece of glass tubing of the same diameter as the end of the drawn-out neck of the flask is pressed closely against the end of this neck, and the joint is made tight by caoutchouc. The flask is then placed in a water bath and very slowly heated to 20°, and after some time to 30°–40°; the gas is collected, by downward displacement, in small dry flasks, or it may be liquefied by passing into small tubes surrounded by snow and salt. The whole operation is best conducted by gas-light (Millon, *J. pr.* 29, 401; Cohn, *J. pr.* 83, 54). If the liquid is prepared each tube should not contain more than 1 or 2 drops; the liquid is frightfully explosive. The gas prepared as above always contains a little Cl and O.—2. According to Jacquelain (*A. Ch.* 30, 339) fairly pure ClO_2 may be obtained by the action of a mixture of equal volumes of conc. H_2SO_4 and water on pure $KClO_3$, in a flask with a long neck, placed in water at 70° so that half the neck is immersed.—3. If a very intimate mixture of 3 pts. finely powdered $KClO_3$ with 13 pts. finely powdered crystallised oxalic acid is warmed in an oil bath to 70° a mixture of ClO_2 and CO_2 is evolved regularly and without danger; five-sixths of the Cl of the $KClO_3$ forms ClO_2 and one-sixth remains as KCl (Calvert a. Davies *C. J.* 11, 193; *v.* also Schacherl, *A.* 206, 75).

Properties.—Yellowish-green gas, condensing (by snow and salt) to a red-brown liquid, and solidifying at about −59° (ether and solid CO_2 *in vacuo*) to hard, brittle crystals, resembling $K_2Cr_2O_7$ in appearance (Faraday, *T.* 1845. 155). Both gas and liquid are frightfully explosive; explosions often occur without any assignable cause. S.G. of liquid ClO_2 about 1·5. B.P. about 9° (Pebal, *A.* 177, 1). In a vessel wholly made of glass, liquid ClO_2 boils at 9·9° under pressure of 730·9 mm. without explosion (Schacherl, *A.* 204, 68). The gas has an irritating odour, resembling that of NO_2; it does not affect litmus paper: it is unchanged in the dark, but decomposes, usually explosively, in sunlight.

Reactions and Combinations.—1. *Easily oxi-*

dised bodies, *e.g.* P, or S, burn in ClO_2, usually with explosion.—2. *Mercury* absorbs the gas and decomposes it with detonation.—3. *Hydrogen* (8 vols. H + 3 vols. ClO_2) decomposes ClO_2 explosively in presence of spongy Pt, or of electric sparks, forming H_2O and HCl (Blundell, *P.* 2, 216; Stadion, *G. A.* 52, 197 a. 339).—4. According to Kammerer (*P.* 138, 404) *bromine* and *iodine* do not react with gaseous ClO_2.—5. Many *organic compounds* cause explosion of ClO_2 at ordinary temperatures. – 6. Liquid ClO_2 explodes when a piece of *potash* is placed in it; if water is present, a mixture of equal equivalents of $KClO_2$ and $KClO_3$ is formed, much heat being produced.—7. Liquid ClO_2 sinks in *water*; on shaking, much gas is given off, an explosion usually takes place, and the water contains $HClO_2$ and $HClO_3$. If the water is kept at 0° yellow crystals are formed which cannot be melted without evolution of considerable quantities of gas (Millon, *A. Ch.* [3] 7, 298). Water at 4° absorbs about 20 times its own volume of gaseous ClO_2, with formation of $HClO_2Aq$ and $HClO_3Aq$ (Millon, *l.c.*); this solution decomposes in sunlight, giving off Cl and O, and after a time only $HClO_4$ remains in solution.—8. Conc. *sulphuric acid* at −18° absorbs about 20 times its own volume of gaseous ClO_2, becoming yellow in colour; on removing the acid from the freezing mixture the colour changes to reddish; at 10°-15° ClO_2, Cl_2O_3 (?), and a mixture of Cl and O in the proportion of 2 vols. to 3 vols., are evolved; when gas ceases to come off, the residue contains $HClO_4$ (Station, *G. A.* 52, 197 a. 339; Millon, *A. Ch.* [3] 7, 298).

Method of Analysis.—(Pebal, *A.* 177, 1; 213, 112). The gas was prepared by gently warming H_2SO_4Aq (1 vol. conc. acid to 2 vols. water) with a mixture of oxalic acid and potassium chlorate; it was washed by passing through a little water, dried by $CaCl_2$, and liquefied in a small glass bulb with two glass necks surrounded by $CaCl_2$ and snow. When about 3 c.c. of the liquid were obtained, the evolution of gas was stopped; one neck of the glass bulb was closed, and the other was connected with a glass tube, furnished with glass stop-cocks, placed in water. The freezing mixture was removed, and gaseous ClO_2 was allowed to pass slowly through the glass tube till all air was removed; the stop-cocks of the tube were then closed, and the temperature of the water and the reading of the barometer were determined. The glass tube full of ClO_2 was surrounded by fine wire gauze (in case an explosion should occur), and the water was gently warmed until decomposition of the gas occurred; the temperature of the water was then allowed to come back to the first reading. The mixed gases, or a portion of them, were then transferred to a similar graduated glass tube, filled with saturated NaClAq containing a little ClAq and placed in a cylinder full of the same solution; this solution absorbs hardly any Cl from a mixture of Cl and O. The volume of Cl in the known volume of the mixed gases was determined by absorption by KIAq. The following results were obtained:

(1) Volume - expansion on decomposition $23{\cdot}9:36{\cdot}44 = 2:3{\cdot}05$;

(2) Ratio of Cl-volume to O-volume $11{\cdot}1:23{\cdot}2 = 1:2{\cdot}09$;

(3) Ratio of O-volume to expansion $24{\cdot}65:12{\cdot}54 = 1{\cdot}96:1$;

that is, 2 vols. chlorine peroxide yields 2 vols. O and 1 vol. Cl. Then from the weights of O and Cl obtained, and the weight of chlorine peroxide used (calculated from the observed S.G. of the three gases) the formula ClO_2 is deduced. It is possible that the gas at low temperatures, or the liquid, may have the composition Cl_2O_4. ClO_2 may also be analysed by allowing the liquid to act on $FeSO_4Aq$ and determining the Fe_23SO_4 and the HCl produced;

$$10FeSO_4Aq + 5H_2SO_4Aq + 2ClO_2$$
$$= 5Fe_23SO_4Aq + 2HClAq + 4H_2O$$

(*v.* Garzarolli-Thurnlackh, *A.* 209, 205).

References.—Stadion, *G. A.* 52, 197 a. 339. Davy, *T.* 1815. 214. Gay-Lussac, *A. Ch.* 8, 408. Soubeiran, *A. Ch.* 48, 113. J. Davy, *N. Ed. P. J.* 17, 49. Millon, *A. Ch.* [3] 7, 298. Calvert a. Davies, *C. J.* 11, 193. Cohn, *J. pr.* 85, 53. Faraday, *T.* 1845. 155. Blundell, *P.* 2, 216. Kammerer, *P.* 138, 404. Pebal, *A.* 177, 1. Garzarolli-Thurnlackh, *A.* 209, 184.

III. CHLORINE TRIOXIDE. Cl_2O_3 (*Chlorous anhydride.*) The existence of this body is very doubtful. The results obtained by Millon, Carius, Schiel, &c. differed considerably: thus Millon could not liquefy the gas he obtained; Schiel and others obtained a dark reddish-brown liquid by passing the gas into a tube in snow and salt. Brandau determined the S.G. of the gas to be 4·07 at 9°, 4·02 at 13°, and 3·17 at 16°; Millon gave the S.G. as 2·65 and Schiel as 2·6 – 2·73. (The calculated S.G. of Cl_2O_3 is 4·109, air = 1.) The gas was analysed by Millon by passing it over hot Cu and determining the $CuCl_2$ formed; Brandau dissolved in water and titrated with KIAq, he also reduced by HNO_2Aq and estimated the Cl. The results cannot be regarded as satisfactory. Garzarolli-Thurnlackh (*B.* 14, 28; more fully, *A.* 209, 184) in 1881 determined the relation between the expansion of the gas on decomposing it by heat and the volume of O thus obtained; he employed Pebal's method for analysis of ClO_2 (*q. v.*); the gas examined was prepared by the action of (1) $KClO_3$ and HNO_3Aq on As_4O_6 (Millon's method), (2) $KClO_3$ and H_2SO_4Aq on C_6H_6 (Carius's method modified by Brandau), (3) $KClO_3$ and HNO_3Aq on sugar (Schiel's method). In every case the volume of O obtained was almost exactly double the total expansion of the gas; but if the gas were Cl_2O_3 the volume of O must be equal to the total expansion, and this result would hold good if free Cl were mixed with the Cl_2O_3. Garzarolli-Thurnlackh concludes that the gas supposed to be Cl_2O_3 by Millon and Brandau was really a mixture of ClO_2, with varying quantities of Cl, a little O, and CO_2.

Preparation of compound said to be Cl_2O_3.—1. Millon (*A. Ch.* [3] 7, 298) used 15 pts. finely-powdered As_4O_6 and 20 pts. powdered $KClO_3$ made into a thin cream with water; to this he added 60 pts. pure HNO_3Aq (free from HCl and H_2SO_4) S.G. 1·33, diluted with 20 pts. H_2O; the mixture was placed in a flask of a size such that the liquid partly filled the neck, an exit tube was attached, and the contents gradually warmed in a water-bath to about 25°. The gas may be dried by $CaCl_2$; it is collected in dry flasks by downward displacement. The flask should be covered with a thick cloth in case of explosion. Slight explosions sometimes occur, but if the process is conducted carefully it is unattended with danger.—2. Schiel (*A.* 109, 319) used a mixture of 2 pts. $KClO_3$, ·6 to ·8 pts. cane sugar, and 3 pts. HNO_3Aq, S.G. 1·3 diluted with 3–4 pts. H_2O; the gas contained CO_2.—3. Carius (*A.* 140, 317; *v.* also Brandau, *A.* 151, 63) dissolved 10 pts. C_6H_6 in 100 pts. conc. H_2SO_4, diluted with 100 pts. H_2O, after cooling added 12 pts. powdered $KClO_3$, and heated to about 50° on a water-bath. The exit tube of the flask was connected with a series of small bulbs containing water; from these the gas passed into a tube kept at −18°; the liquefied oxide was separated from crystals of hydrated chloric acid (*q. v.*). About 5 7 c.c. liquid was obtained from 54 grams $KClO_3$; the liquid contained a little water and traces of ClO_2 and $HClO_3$.

Properties of the supposed compound.—The properties said to belong to Cl_2O_3 resemble those which characterise ClO_2; the former is however less explosive. It is described as a greenish-yellow gas, condensing to a dark red-brown liquid; S.G. about 1·5; the liquid volatilises at about 0°, the latter portions boiling at 8° 9°. The gas is decomposed into Cl and O at about 57° with slight explosion. In contact with most non-metals, and with Te and As detonation occurs. Pb, Cu, Sn, Sb, Ag, Zn, and Fe are unchanged in the gas; Hg absorbs it. One volume H_2O absorbs $8\frac{1}{2}$ vols. of the gas at 8°; the solution contains $HClO_2$, and after a time also $HClO_3$. Brandau says that if the water is at 0°, a solid hydrate of $HClO_2$ containing from 50 to 67·5 p.c. H_2O is produced.

References. — Millon, *A. Ch.* [3] 7, 298; De Vrij, *A.* 61, 248; Schiel, *A.* 108, 128; 109, 317; 112, 73; 116, 115; Carius, *A.* 140, 317; 142, 129; 143, 321; Brandau, *A.* 151, 340; Garzarolli-Thurnlackh, *B.* 14, 28; *A.* 209, 184.

M. M. P. M.

CHLORINE, OXY-ACIDS OF.—Four compounds are known, HClO, $HClO_2$, $HClO_3$, and $HClO_4$. The anhydride of HClO, viz. Cl_2O, is known; the anhydride of $HClO_2$, viz. Cl_2O_3, is generally stated to be known, but the evidence is not conclusive (*v.* CHLORINE TRIOXIDE). Of the acids, only $HClO_4$ has been obtained in definite form apart from water. Aqueous solutions of HClO and $HClO_2$ are easily decomposed on heating, giving $HClO_3Aq$ and HClAq; the most conc. solution of $HClO_3Aq$ obtained contains the acid and water in the ratio $HClO_3{:}4\frac{1}{2}H_2O$, this solution decomposes on heating yielding $HClO_4Aq$, Cl, and O; $HClO_4Aq$ is stable, it may be concentrated by distillation until crystals of $HClO_4.H_2O$ are obtained; by carefully heating these crystals the acid $HClO_4$ is formed, this acid is very easily decomposed with explosion. The following thermal data are given by Thomsen (*Th.* 2, 400):—

$$[H,Cl,Aq] = 39{,}315$$

$$\text{Diff.} = -9{,}385$$

$$[H,Cl,O,Aq] = 29{,}930$$

$$\text{Diff.} = -5{,}990$$

$$[H,Cl,O^3,Aq] = 23{,}940$$

These numbers would lead us to expect that neither HClOAq nor $HClO_3Aq$ would be produced by the direct addition of O to HClAq; nor should we expect to form $KClO_3Aq$ by adding O to KClAq, for $[KClAq,O^3] = -15{,}370$ (Thomsen); the production of HClOAq by the direct combination of Cl and O in presence of H_2O is also improbable, considering that $[Cl^2,O,Aq] = -8{,}490$ (Thomsen). Cl and O do not unite directly, but if a moderately basic oxide, *e.g.* HgO or ZnO, is acted on by Cl and H_2O, HClOAq is produced; if a strongly basic oxide, *e.g.* K_2O or Na_2O, is used, a salt of HClO is formed in solution. Odling (*Ph.* [2] 1, 469) says that HClOAq is formed when a current of air laden with HCl is passed into a warm solution of $K_2Mn_2O_8$ containing H_2SO_4. HClOAq is also said to yield $HClO_4Aq$ by the action of ozone. In the ordinary processes whereby $HClO_3Aq$ and $HClO_4Aq$ are obtained from HClOAq (or salts of the higher acids from salts of HClO) much heat is produced in the decomposition of the lower acid, or salt, and O is set free at the same time; under these conditions the higher acids, or salts, are formed. When KClOAq is heated KClAq and $KClO_3Aq$ are produced; when $KClO_3$ is heated, O is evolved and $KClO_4$ and KCl are produced; on raising the temperature KCl remains and all the O is evolved. Thomsen (*Th.* 2, 145) gives the following thermal values for the possible reactions between Cl and K_2O:—

$$[Cl^6,3K^2OAq] = \begin{cases} 73{,}935 \text{ if } 3KClOAq + 3KClAq \\ 97{,}945 \text{ if } KClO_3Aq + 5KClAq \\ 113{,}315 \text{ if } \quad 3O + 6KClAq \end{cases}$$

are formed.

Chloric acid is as strong an acid, *i.e.* its affinity is as great, as hydrochloric acid (*v.* AFFINITY, vol. i. pp. 82, 83) (*comp.* BROMINE, OXY-ACIDS OF. *v.* also HALOGEN ELEMENTS).

Detection and Estimation of salts of HClO, $HClO_2$, $HClO_3$, and $HClO_4$.

I. Salts of HClO in solution react as oxidisers much in the same way as ClAq; on adding a little extremely dilute HNO_3Aq and distilling, a dilute solution of HClOAq is obtained which (1) bleaches indigo at once, but does not bleach if As_4O_6Aq is present, (2) gives a brownish pp. of $HgO.HgCl_2$ when shaken with Hg, (3) with SO_2Aq forms a solution containing 1 equivalent HCl to 2 equivalents H_2SO_4 ($HClOAq + SO_2Aq + H_2O = H_2SO_4Aq + HClAq$). Hypochlorites may be estimated by titration with KIAq and $Na_2S_2O_3Aq$.

II. Salts of $HClO_2$ in solution react very much as mixtures of chlorates and chlorides; they are decomposed by H_2SO_4Aq (1 acid to 8–10 water) with formation of a yellow colour probably due to ClO_2 and Cl, whereas a mixture of chloride and chlorate is not decomposed. They bleach acidulated indigo at once even in presence of As_4O_6Aq. With SO_2Aq a solution is formed containing HCl and H_2SO_4 in the ratio $HCl{:}2H_2SO_4$ ($HClO_2Aq + 2SO_2Aq + 2H_2O = 2H_2SO_4Aq + HClAq$). Chlorites may be estimated by allowing them to oxidise a standardised acidulated solution of $FeSO_4$, and determining the residual $FeSO_4$ by $K_2Mn_2O_8Aq$.

III. Salts of $HClO_3$ in solution do not bleach acidulated dilute indigo solution in the cold until a little SO_2Aq is added (Cl is then set free);

they do not separate I at once from KIAq. They are decomposed by digestion with warm conc. HClAq; salts of $HClO_4$ are not. Chlorates may be estimated by reduction to chlorides, by Zn and H_2SO_4Aq, or by a Cu-Zn couple (*v.* Bothamley and Thompson, *C. J.* 53, 159). They may be separated from chlorites by conversion into K salts, and repeated evaporation *in vacuo* (*v.* CHLOROUS ACID AND CHLORITES). $KClO_3$ is fairly soluble in water at 15° (S = 6), and $KClO_4$ is nearly insoluble (S = 1·6); $KClO_4$ is insoluble in alcohol containing a little $K.C_2H_3O_2$; a method of separation of $KClO_3$ and $KClO_4$ may be based on these facts.

IV. Salts of $HClO_4$ are not decomposed by digestion with conc. HClAq at 100°; their solutions do not bleach acidulated indigo even in presence of SO_2Aq, nor are they reduced by a Cu-Zn couple at 100°. Perchlorates may be estimated by converting them into $KClO_4$ and determining the O in them by heating, and the K and Cl in the residue by the usual methods.

I. HYPOCHLOROUS ACID AND HYPOCHLORITES. HClOAq; MClOAq. In 1788 Berthollet obtained a liquid with bleaching properties by the action of chlorine on aqueous alkalis; Berthollet thought the liquid contained a compound of the alkali and chlorine, the latter being then regarded as oxidised hydrochloric acid. Berzelius supposed that a mixture of alkali chloride and chlorite was formed. In 1834 Balard proved that the bleaching liquid contained a salt of a new acid (Berthollet, *Statique Chimique*, 2, 183; Berzelius, *P.* 12, 529; Balard, *A. Ch.* 57, 225). The acid is known only in aqueous solutions; one salt $Ca(ClO)_2.xH_2O$ has been obtained as a solid.

Formation.—1. By the action of Cl on ZnO in presence of water; $ZnCl_2Aq$ is formed at the same time.—2. By the action of Cl on (1) $CaCO_3$ suspended in water; $(CaCO_3 + H_2O + Aq + 2Cl_2$
$= CaCl_2Aq + 2HClOAq + CO_2)$:
(2) Na_2CO_3Aq; $(2Na_2CO_3Aq + 2H_2O + 2Cl_2$
$= 2NaClAq + 2HClOAq + 2NaHCO_3Aq$; then
$2NaHCO_3Aq + 2Cl_2$
$= 2NaClAq + 2CO_2 + 2HClOAq)$:
(3) Na_2SO_4Aq; $(Na_2SO_4Aq + H_2O + Cl_2$
$= NaHSO_4Aq + NaClAq + HClOAq)$.—3. By the action of Cl on $AgCO_3$ suspended in water; AgCl is also formed.—4. By the action of Cl on CaO_2H_2Aq; CaO_2Cl_2 and $CaCl_2$ are probably formed (*v* p. 17); when to an aqueous solution of this product as much very dilute HNO_3Aq is added as suffices to convert less than the half of the Ca into $Ca2NO_3$, and the liquid is distilled, dilute HClOAq is obtained (Gay-Lussac, *A.* 43, 153; Schorlemmer, *B.* 6, 1509; Kopfer, *C. J.* [2] 13, 713).—5. By passing Cl_2O into H_2O, HClOAq is formed (*v.* CHLORINE MONOXIDE).—6. Addition of H_2O_2Aq (containing 2·45 p.c. H_2O_2) to a large excess of ClAq produces HClOAq, according to Fairley (*B. A.* 1874, 57); if much H_2O_2 is added, the HClOAq is decomposed forming HClAq, H_2O, and evolving O.—7. According to Odling (*J.* 1860. 65) HClOAq is formed by leading air laden with HCl into a warm solution of $K_2Mn_2O_8$ containing H_2SO_4Aq, or into a mixture of MnO_2 and H_2SO_4Aq.—8. HClOAq is also formed, along with other salts, by the action of Cl on aqueous solutions of Na_2HPO_4, $FeSO_4$, $ZnSO_4$, $MnSO_4$, $CuSO_4$, $Zn(C_2H_3O_2)_2$.—9. Alkali salts of HClO are produced by electrolysis of NaClAq or KClAq (Lidoff a. Tichomiroff, *J. R.* 1882. 212).

Preparation.—A flask of somewhat under 1000 c.c. capacity, with a good-fitting glass stopper, is filled with air-free Cl in the dark; ppd. HgO, which has been heated to 300° and cooled, suspended in a little H_2O, is added, in the proportion of 15 grams to 1 litre Cl; the flask is shaken for about 15 minutes, and the liquid is poured off from the Hg_2OCl_2 formed: this solution contains from 2 to 3 p.c. of HClO (Carius, *A.* 126, 196). If the Cl used contains much air the reaction proceeds very slowly; if the HgO has not been heated to 300° much $Hg2ClO_3$ is formed. $2HgO + 2Cl_2 + H_2O + Aq = HgO.HgCl_2 + 2HClOAq$. The solution of HClOAq is best kept in contact with a little HgO; any Cl set free is thus continually converted into HClO.

Properties.—An aqueous solution of HClO smells like Cl_2O. It is very easily decomposed into Cl and $HClO_3Aq$; in sunlight this change proceeds rapidly, the more conc. the solution the more rapid is the decomposition, and traces of $HClO_4$ are also formed (Popper, *A.* 227, 161). A dilute solution of HClO may be distilled with partial decomposition, the distillate is richer in HClO; Gay-Lussac found that, on distilling a dilute solution to one-half, the distillate contained five-sixths of the total HClO (*C. R.* 14, 927). HClOAq is a monobasic acid; added to KOHAq or $Ca(OH)_2Aq$, KClOAq or $Ca(ClO)_2Aq$ is formed. Thomsen gives the heat of neutralisation as [HClOAq, NaOHAq] = 9,980, which is about $\frac{2}{3}$ of the value of the heat of neutralisation of one of the stabler monobasic acids (*e.g.* HCl, $HClO_3$, HNO_3), and is a little greater than the value for HSHAq, viz., 7,740. HClOAq does not dissolve bases insoluble in water, nor does it decompose the carbonates of these bases.

Reactions.—1. HClOAq acts generally as an *oxidiser*; it easily parts with O while HClAq remains. Thus, As is rapidly oxidised with evolution of light; P, S, Se, Br, I are converted to H_3PO_4Aq, H_2SO_4Aq, &c., even by dilute HClOAq; lower oxides or salts are converted into higher, *e.g.* SO_2Aq to H_2SO_4Aq, FeO to Fe_2O_3, As_2O_3Aq to As_2O_5Aq, $FeSO_4Aq$ to $Fe_2(SO_4)_3Aq$, Fe_2Cl_6Aq, and Fe_2O_3, $MnSO_4Aq$ to MnO_2; sulphides yield sulphates, *e.g.* H_2SAq gives H_2SO_4Aq and S; NH_3 gives N, H_2O, and NH_4ClAq; HCl forms H_2O and Cl. The quantity of the acid expressed by the formula HClO oxidises the same mass of an oxide &c. as can be oxidised by Cl_2 in presence of H_2O; thus

$$MnO + H_2O + \left\{\begin{matrix}Cl_2\\ HClO\end{matrix}\right. = MnO_2 + \left\{\begin{matrix}2HCl\\ HCl + H_2O.\end{matrix}\right.$$

2. On many *carbon compounds* HClOAq acts partly as an oxidising, partly as a chlorinating, agent; *e.g.* $H_2C_2O_4Aq + HClOAq = 2CO_2 + H_2O + HClAq$. Some organic compounds combine with the acid: *e.g.* $C_6H_6 + 3HClOAq = C_6H_6Cl_3(OH)_3$, $C_2H_4 + HClOAq = C_2H_4ClOH$.—3. *Indigo* solution, and various other vegetable colours, are rapidly bleached by HClOAq; one formula-weight of HClO in solution exerts as great a bleaching action as Cl_2 ($HClOAq = HClAq + O$; $Cl_2 + H_2O = 2HCl + O$).—3. HClOAq

is said to be oxidised to $HClO_4Aq$ by *ozone* (Fairley, *B. A.* 1874. 58).

Hypochlorites are very easily decomposed; even in dilute solutions boiling suffices to convert them into chlorides and chlorates, in conc. solutions boiling produces chlorides and O. Their solutions are also decomposed by heating with Co_2O_3, CuO, MnO_2 &c., O is evolved and chlorides remain; *e.g.* $Ca(ClO)_2Aq + Co_2O_3 = CaCl_2Aq + Co_2O_3 + O_2$ (CoO_3 is perhaps formed and again reduced to Co_2O_3 with evolution of O; Winkler, *J. pr.* 98, 340). As $Ca(OCl)_2Aq$ is formed by the action of Cl on CaOAq, it is easy to obtain O by leading Cl into strong warm milk of lime containing a little Co_2O_3 ($Co.2NO_3$ is used). Solutions of KClO and NaClO, along with KCl and NaCl, are obtained by leading Cl into cold dilute KOHAq or NaOHAq. Solutions of hypochlorites bleach rapidly on addition of a little HNO_3Aq, H_2SO_4Aq, HClAq, or even CO_2Aq; these solutions act as oxidisers towards P, S, I, &c. As the hypochlorites are so easily decomposed it is difficult to obtain them, even in solution, free from chlorides. Kingzett (*C. J.* [2] 13, 401) obtained crystals of nearly pure calcium hypochlorite, $CaO_2Cl_2.xH_2O$, by exhausting bleaching powder with cold H_2O, filtering, and placing the filtrate *in vacuo* over conc. H_2SO_4. The crystals very easily decomposed, even by drying *in vacuo*, with evolution of Cl. The greater part of the Cl was lost by heating the moist crystals to 100°, the residue probably contained chlorate, it also contained much carbonate. The crystals dissolved in H_2O; this solution was decomposed by CO_2 with evolution of most, but not all, of the chlorine. That an aqueous solution of bleaching powder contains CaO_2Cl_2 has been confirmed by O'Shea (*C. J.* 43, 422), who proved that when such a solution is diffused without a membrane the diffusate contains considerably less active Cl (*i.e.* Cl which is so combined with Ca and O that it is capable of bleaching), and the residue considerably more active Cl than the original liquid, in proportion to the Cl or $CaCl_2$; that is, diffusion sufficed to render the diffused liquid relatively poorer in active Cl and richer in chloride.

Bleaching powder.—Cl is absorbed by slaked lime and the product possesses strong bleaching properties. Gay-Lussac regarded bleaching powder as containing $CaCl_2O_2$ and $CaCl_2$ in the ratio $CaCl_2O_2:CaCl_2$. Odling (*Manual of Chem.* 1, 56) suggested the composition Ca.OClCl, chiefly because bleaching powder is not deliquescent nor is $CaCl_2$ removed from it by treatment with alcohol. Göpner (*J. pr.* [2] 7, 441) asserted bleaching powder to be a compound of CaO with Cl, and to have the composition $CaO.Cl_2$. Stahlschmidt (*B.* 8, 869) suggested the composition Ca.OH.OCl. Bleaching powder prepared by the action of pure dry Cl on pure dry $Ca(OH)_2$ always contains some $Ca(OH)_2$; but the quantity of this is variable and can be much diminished by repeated treatment with dry Cl, the $Ca(OH)_2$ is not therefore an essential part of the bleaching compound (*v.* Kopfer, *C. J.* [2] 13, 713; O'Shea, *C. J.* 43, 422; Lunge a. Schäppi, *D. P. J.* 237, 63). That $CaCl_2$ is not present as such in bleaching powder is shown by the facts that it is not deliquescent, that when treated with small successive quantities of water the first washings contain much less Cl than would be the case were $CaCl_2$ present in the liquid, and that in the presence of a little moisture almost the whole of the Cl can be removed from bleaching powder by the action of CO_2 (Lunge a. Schäppi, *D. P. J.* 237, 63; *v.* also Lunge a. Naef, *B.* 16, 840).

The composition $CaO.Cl_2$ assigned by Göpner to the bleaching compound in bleaching powder was disproved by the experiments of Kopfer (*C. J.* [2] 13, 713), who showed that when an extremely dilute mineral acid (HCl, HNO_3, or H_2SO_4) is added to a solution of bleaching powder, in quantity sufficient to saturate all the lime and the $Ca(OCl)_2$ present—calculated on the assumption that the active (bleaching) Cl exists as $Ca(OCl)_2$—and the liquid is distilled, almost the theoretical quantity of HClO is obtained in the distillate. The formula Ca.OH.OCl given to the bleaching compound by Stahlschmidt assigns a limit to the amount of active Cl, *i.e.* Cl available for bleaching, in the powder: Stahlschmidt represents the formation of the bleaching powder thus—$3Ca(OH)_2 + 2Cl_2 = 2Ca.OH.OCl + CaCl_2 + 2H_2O$. The strongest bleaching powder cannot therefore contain more than about 33 p.c. of available Cl; but Lunge a. Schäppi (*D. P. J.* 237, 63) prepared bleaching powder containing 43·4 p.c. available Cl. Moreover, according to Stahlschmidt's view, when water acts on bleaching powder, the reaction is $2Ca.OH.OCl = Ca(OH)_2 + CaO_2Cl_2$; therefore no bleaching powder can be represented as containing CaO_2Cl_2 and $CaCl_2$ in a greater ratio to $Ca(OH)_2$ than 1:1:1. Now O'Shea (*C. J.* 43, 422) determined the ratio of $Ca(OCl)_2$ (supposing all available Cl to exist in this form): $CaCl_2:Ca(OH)_2$ in six samples of bleaching powder made from pure $Ca(OH)_2$; in 2 out of the 6 samples the ratio was $3CaO_2Cl_2:3CaCl_2:2Ca(OH)_2$. Finally O'Shea removed any $CaCl_2$ present as such from various samples of bleaching powder, prepared from pure $Ca(OH)_2$ by repeated treatment with alcohol, and determined the total CaO, the total Cl, and the available Cl, in the residue, *i.e.* in the bleaching compound; the results in every case were—(1) CaO : total Cl = 1:2; (2) available Cl : total Cl = 1:2; (3) CaO : available Cl = 1:1.

Stahlschmidt's formula Ca.OH.OCl requires for (1) the ratio 1:1; for (2) 1:1; for (3) 1:1.

Gay-Lussac's formula CaO_2Cl_2 requires for (1) the ratio 1:2; for (2) 1:1; for (3) 1:2.

Odling's formula Ca.OCl.Cl requires for (1) the ratio 1:2; for (2) 1:2; for (3) 1:1.

The experiments of Kingzett already referred to (*v. supra*) showed that when water acts on bleaching powder CaO_2Cl_2 is contained in the solution. There can be little doubt that the formula Ca.OCl.Cl better expresses the composition and properties of the bleaching compound in bleaching powder than any other formula yet suggested; and that the reaction which occurs when water is added to this compound is $2Ca.OCl.Cl + Aq = CaO_2Cl_2Aq + CaCl_2Aq$.

II. Chlorous acid and Chlorites. $HClO_2Aq$; $MClO_2$. Chlorous acid is known only in aqueous solution; it is indeed doubtful whether even a solution of $HClO_2$ has been obtained free from $HClO_3$. $KClO_2$ may be prepared by adding an aqueous solution of ClO_2 of known strength to the proper quantity of KOHAq, evaporating at 45°-50° *in vacuo*, separating from $KClO_3$ which crystallises out, repeating the evaporation and separation of $KClO_3$, then adding alcohol to the mother liquor, evaporating *in vacuo*, and collecting the second crop of crystals which form (Garzarolli-Thurnlackh a. J. Hayn, *A.* 209, 203). $HClO_2Aq$ could not be obtained by the action of acids on this salt. When the gas obtained by acting on $KClO_3$ with HNO_3Aq and As_4O_6 is led into water, a yellowish-red acid solution is obtained, which on warming, or on exposure to sunlight, contains HCl and $HClO_3$. This solution when freshly prepared is generally supposed to be $HClO_2Aq$; but the experiments of Garzarolli-Thurnlackh (*v.* CHLORINE TRIOXIDE) render it almost certain that the gas obtained as above is a mixture of ClO_2 and Cl, and that the solution contains both $HClO_2$ and $HClO_3$.

The solution prepared as described reacts with many metals; *e.g.* Hg forms an oxychloride, Cu a mixture of $CuCl_2$ and $Cu(ClO_3)_2$, Zn and Pb form chlorides and probably chlorites, and finally chlorates; with the lower salts of Sn, Fe, Hg, &c., the solution reacts to form higher salts of these metals; As_2O_3Aq is not oxidised to As_2O_5Aq; HCl decomposes the solution forming Cl and H_2O, HIAq gives HCl and I; HNO_2Aq is oxidised to HNO_3Aq; SO_2Aq is oxidised to H_2SO_4Aq. According to Brandau (*A.* 151, 340) if the gas supposed to be Cl_2O_3 is led into H_2O at 0° a solid hydrate of $HClO_2$ is obtained; when pressed between paper the hydrate is a lustrous mass remaining unmelted at 10°, and volatilisable without residue. Two specimens gave 50 and 67·5 p.c. water respectively.

Chlorites. Very few of these salts have been prepared. *Potassium chlorite*, $KClO_2$, prepared as above described, forms needles, which deliquesce after standing some time in the air. The *silver* and *lead* salts, $AgClO_2$ and $Pb(ClO_2)_2$ are obtained by adding $AgNO_3Aq$ and $Pb(C_2H_3O_2)_2Aq$ respectively, to $KClO_2Aq$. $AgClO_2$ crystallises from hot H_2O in greenish-yellow scales; it is slowly decomposed in direct sunlight; SO_2Aq rapidly reduces to AgCl; dilute H_2SO_4Aq evolves a gas the colour and smell of ClO_2. $KClO_2Aq$ quickly oxidises $FeSO_4Aq$; $KClO_2$ mixed with S and rubbed ignites the S. $Pb(ClO_2)_2$ after washing with hot H_2O forms greenish-yellow scales; slightly soluble in hot H_2O; reactions similar to those of $KClO_2$; soluble in KOHAq. This solution is reduced by SO_2Aq to $PbSO_4$ and $PbCl_2Aq$ (Garzarolli-Thurnlackh a. J. Hayn, *A.* 209, 203). Millon (*A. Ch.* [3] 7, 298) described $Ba(ClO_2)_2$ and $Sr(ClO_2)_2$ as very soluble salts; probably the salts contained Ba and $Sr(ClO_3)_2$.

III. CHLORIC ACID AND CHLORATES. $HClO_3Aq$; $MClO_3$. An aqueous solution of $HClO_3$ is formed when ClO_2Aq is exposed to sunlight, or is heated. $KClO_3$ and $NaClO_3$ are produced by electrolysis of KClAq and NaClAq respectively: carbon electrodes are employed (Lidoff a. Tichomiroff, *J. R.* 1882. 341).

Preparation.—1. $Ba(ClO_3)_2$ is obtained by dissolving 3 pts. crystallised $(NH_4)_2SO_4$ and 3 pts. $KClO_3$ in 15 pts. hot H_2O, evaporating to a thin syrup, digesting for a day at a gentle heat with alcohol (80 p.c.), filtering from K_2SO_4, adding BaOAq, evaporating, and crystallising (Wittstein; *v.* also Böttger, *A.* 57, 138). A weighed quantity of the crystals of $Ba(ClO_3)_2$ is dissolved in H_2O; a quantity of dilute H_2SO_4Aq exactly sufficient to pp. all the Ba as $BaSO_4$ is added, little by little; the liquid is filtered—the filtrate must give no pp. either with BaOAq or H_2SO_4Aq - and the filtrate is concentrated *in vacuo* over H_2SO_4.—2. Hot $KClO_3Aq$ is decomposed by excess of H_2SiF_6Aq; after cooling, the liquid is filtered from K_2SiF_6 and evaporated over H_2SO_4 and KOH *in vacuo*; the excess of H_2SiF_6 volatilises and $HClO_3Aq$ remains.

Properties. - By evaporation *in vacuo* of dilute $HClO_3Aq$, a somewhat oily, colourless, strongly acid, liquid is obtained, with S.G. 1·282 at 14°; according to Kämmerer this liquid contains $HClO_3$ and H_2O in the ratio $HClO_3{:}7H_2O$; the same chemist says that if this liquid remains longer *in vacuo*, sudden evolution of Cl and O occurs, and $HClO_3.4\frac{1}{2}H_2O$ remains (*P.* 138, 390). The strongest solution of $HClO_3$ does not solidify at −20°. $HClO_3Aq$ reddens litmus paper and then bleaches it; paper or linen soaked in fairly conc. acid and dried takes fire. Heated to about 40° the solution decomposes into $HClO_4Aq$, Cl, O, and H_2O (Serullas, *A. Ch.* 45, 204 a. 270). Thomsen gives these thermal values $[H,Cl,O^3,Aq]$ 23,940, but $[Cl^2,O^5,Aq] = -20,480$; $[HClO^3Aq, KOHAq] = 13,760$. The affinity of $HClO_3Aq$ is equal to that of the strongest acids (*v.* AFFINITY, vol. i. pp. 82, 83).

Reactions. —1. *Zinc* and *iron* dissolve in $HClO_3Aq$ with evolution of H.—2. *Iodine* is oxidised to HIO_3Aq.—3. Oxidisable *oxygen compounds* are converted into higher compounds, *e.g.* SO_2Aq gives H_2SO_4Aq, Cl, and H_2O; H_3PO_3Aq gives H_3PO_4Aq. —4. *Chlorhydric acid* forms H_2O and Cl. 5. *Sulphuretted hydrogen* produces H_2SO_4Aq and S. — 6. *Iodine* gives HIO_3Aq; *bromine* only traces of $HBrO_3Aq$ (Kämmerer, *P.* 138, 399). 7. By *electrolysis* $HClO_3Aq$ yields first $HClO_2Aq$, and then Cl (Buff, *A.* 110, 257). —8. *Heated* above 40° $HClO_3Aq$ decomposes into Cl, O, H_2O, and $HClO_4Aq$.

Chlorates. $HClO_3Aq$ acts as a monobasic acid. Normal chlorates are all soluble in water; $KClO_3$ is less soluble than the others. Chlorates may be prepared by acting on $Ba(ClO_3)_2Aq$ with the sulphate of the metal whose chlorate is required; many are also obtained by the action of the metallic oxide, or carbonate, on $HClO_3Aq$. Chlorates easily part with their O when heated; they act therefore as oxidisers (*v. Potassium chlorate*). Aqueous solutions are not, however, very easily reduced (*e.g.* H_2S has no action); boiled with P, chlorides are formed (Slater, *J. pr.* 60, 247); chlorates in solution are also reduced by Zn and dilute H_2SO_4Aq, and by a Cu-Zn couple. Fusible chlorates detonate when rubbed with easily combustible bodies, *e.g.* S or Sb_2S_3; sometimes violent explosions occur. H_2SO_4Aq decomposes chlorates with evolution of ClO_2 and Cl; HClAq evolves *euchlorine*, which is a mixture of ClO_2 and Cl. Solutions of chlorates do not bleach; addition of a little SO_2Aq liberates Cl and bleaching occurs.

Ammonium chlorate. $NH_4.ClO_3$. By adding NH_3Aq, or $(NH_4)_2CO_3Aq$, to $HClO_3Aq$; or $(NH_4)_2CO_3Aq$ to $Ba(ClO_3)_2Aq$ and filtering; or

$(NH_4)_2SiF_6Aq$ to $KClO_3Aq$ and filtering; the solution in each case is evaporated, the salt separates in needles. Soluble in H_2O, and alcohol; sublimes somewhat above 100°; at higher temperature decomposes to Cl, N_2O, and H_2O.

Barium chlorate.—By adding BaOAq, or $BaCO_3$, to $HClO_3Aq$. Thompson (*P. M.* [3] 31, 510) mixes solutions, each in the minimum of water, of 122 parts $KClO_3$ and 167 parts $NH_4.H.C_4H_4O_6$, removes $K.H.C_4H_4O_6$, adds alcohol, filters, decomposes the $NH_4.ClO_3Aq$ by boiling with freshly ppd. $BaCO_3$, filters and crystallises. (*v.* also Bottger, *A.* 57, 138; Brandau, *A.* 151, 361; Bolly a. Merz, *D. P. J.* 153, 358). Crystallises in 4-sided plates. S. (0°) 22·8; (40°) 52·1; (116°) 195; (135°) 287·4; (146°) 365·6; (180°) 522·6 (Tilden a. Shenstone, *T.* 175, 23).

Calcium chlorate. $Ca(ClO_3)_2$. Prepared like $Ba(ClO_3)_2$. Very deliquescent and difficult to crystallise.

Copper chlorate. $Cu(ClO_3)_2.6H_2O$. By dissolving CuO in $HClO_3Aq$ and evaporating. Green, deliquescent, octahedra; soluble in alcohol; decomposed at 100° probably forming a basic salt (Wächter, *A.* 52, 233; *v.* also Casselmann, *Fr.* 4, 24).

Lead chlorate. $Pb(ClO_3)_2$. By saturating $HClO_3Aq$ with PbO, and evaporating; hot solutions deposit rhombohedral deliquescent $Pb(ClO_3)_2.H_2O$ (Wächter, *A.* 52, 233).

Magnesium chlorate. $Mg(ClO_3)_2$. Obtained as, and closely resembles, $Ca(ClO_3)_2$.

Mercury chlorates. (1) $HgClO_3$; columnar crystals, soluble in H_2O and alcohol; by dissolving Hg_2O in $HClO_3Aq$; heated, gives HgCl, Hg, and O. (2) $Hg(ClO_3)_2$ crystallises from solution of HgO in warm $HClO_3Aq$ in needles. S. (about 15°) 25. Decomposed by heat to O, HgCl, $HgCl_2$, and a little HgO.

Potassium chlorate. $KClO_3$. By passing Cl into warm milk of lime containing KCl, and crystallising from the more soluble $CaCl_2$; purified by recrystallisation, or by rubbing with water to a thick cream, and washing with H_2O until KCl is removed (*v.* Lunge, *D. P. J.* 189, 488; Hunt, *B.* 5, 229). White, pearly, monoclinic plates. S.G. 2·35 (Kremers, *P.* 97, 1; 99, 25). S. (0°) 3·3; (15°) 6; (35°) 12; (50°) 19; (75°) 36; (104·8° = B.P.) 60. S. (120°) 73·7; (136°) 98·9; (160°) 148; (190°) 183 (Tilden a. Shenstone, *T.* 175, 23). S.G. of $KClO_3Aq$ at 19·5° (Kremers, *P.* 96, 62; Gorlach, *Fr.* 8, 290) 1 p.c. $KClO_3$ = 1·007; 2 p.c. 1·014; 3 p.c. 1·02; 4 p.c. 1·026; 5 p.c. 1·033; 6 p.c. 1·039; 7 p.c. 1·045; 8 p.c. 1·052; 9 p.c. 1·059; 10 p.c. 1·066. S. (alcohol) as follows: Gerardin (*A. Ch.* [4] 5, 129).

M.P. about 359° (Carnelley, *C. J.* [2] 18, 277). Heated to about 400° evolution of O begins; if the temperature is not increased, evolution of O ceases when KCl and $KClO_4$ are formed (*v.* PERCHLORIC ACID; *Preparation*, p. 20); if the temperature is increased the whole of the O is removed and KCl remains; when the temperature is lower than that at which $KClO_4$ is decomposed the reaction approximates to that represented by the equation $8KClO_3 = 5KClO_4 + 3KCl + 2O_2$ (Teed, *C. J.* 51, 283; Frankland a. Dingwall, *C. J.* 51, 274). If ½ pt. ppd. MnO_2, Fe_2O_3, CuO, or spongy Pt, is mixed with $KClO_3$, O is evolved at a much lower temperature; about 110°–120° with Fe_2O_3, 200°–205° with MnO_2, 230°–235° with CuO, 260°–270° with Pt black. The more finely divided the CuO the lower is the temperature at which evolution of O begins; the temperature is lowered by so little as $\frac{1}{500}$th part of very finely divided CuO, MnO_2, or Fe_2O_3, but the greater the quantity of the foreign body the more rapid is the evolution of O (Mitscherlich, *P.* 55, 220; Wiederhold, *P.* 116, 171; 118, 186; Baudrimont, *J. Ph.* [4] 14, 81 a. 161). $KClO_3$ is an energetic oxidiser; mixed with easily oxidised bodies, *e.g.* S, P, Sb_2S_3, and heated or rubbed, or sometimes even exposed to direct sunlight, explosions occur. Charcoal, S, Sb, Sb_2S_3, finely divided Fe, As, very fine Cu, &c. dropped on to molten $KClO_3$, burn with production of much light (Bottger, *A.* 57, 138). Conc. $KClO_3Aq$ boiled with P produces KClAq, K_2HPO_4Aq, and K_2HPO_3Aq: with As, KClAq and K_2HAsO_4Aq are formed (Slater, *J. pr.* 60, 247). For the action of acids on $KClO_3$ *v.* CHLORINE, OXIDES OF; CHLORINE PEROXIDE, and CHLORINE TRIOXIDE.

Rubidium chlorate. $RbClO_3$. By decomposing Rb_2SO_4Aq by $Ba(ClO_3)_2Aq$. Small trimetric crystals. S. (4·7°) 2·8; (13°) 3·9; (18·2°) 4·9; (19°) 5·1 (Reissig, *A.* 127, 33).

Silver chlorate. $AgClO_3$. A slow stream of Cl is passed into H_2O containing Ag_2O or Ag_2CO_3 in suspension; liquid is decanted from AgCl and is again treated with Cl; after standing for some time at 60°, to convert any AgClO into $AgClO_3$, liquid is evaporated at 100° (Stas, *Chem. Propert.* 90). White, opaque, non-deliquescent, trimetric, crystals. S.G. 4·93 (Schneider, *P.* 106, 226; 107, 113). S. (about 15°) 10; (about 80°–100°) 50: insoluble in alcohol. Decomposed by Cl to AgCl while $HClO_4$ remains in solution; gives AgCl and O on heating; mixed with S explodes more easily than $KClO_3$. A double salt $KClO_3.AgClO_3$ is formed by heating equivalent quantities of $KClO_3Aq$ and $AgClO_3$ to 200° in a closed tube (Pfaundler, *C. C.* 1862. 849).

Sodium chlorate. By action of Cl on warm NaOHAq; better by $KClO_3Aq + Na_2SiF_6Aq$.

S.G. of alcohol ·9904		S.G. 9793		S.G. ·9573		S.G. ·939		S.G. ·8967		S.G. ·8429	
S.	at t°	S.	at t°	S.	at t°	S.	at t°	S.	at t°	S.	at t°
4·9	13°	3·2	14°	1·9	13°	1·1	14·5°	·46	12°	·09	25
7·5	25	5·4	26	2·7	20	2·2	28	1·28	31	·12	34
10·2	35	7·9	38	4·3	36	3·4	40	1·95	43	·24	56
13·6	44	12·2	51	7·9	55	4·3	50	8·10	58	·82	64
16·2	50	17·5	68	10·5	63	7·6	67				

S. (0°) 82; (40°) 123·5; (100°) 204 (Kremers, *P.* 97, 1; 99, 25). S. (alcohol, 83 p.c. 15°) 3. Resembles $KClO_3$.

Strontium chlorate. $Sr(ClO_3)_2.8H_2O$. Prepared as $Ba(ClO_3)_2$. Deliquescent needles; soluble in alcohol (Souchay, *A.* 102, 381).

Zinc chlorate. $Zn(ClO_3)_2$. By dissolving $ZnCO_3$ in $HClO_3Aq$, or decomposing $ZnSiF_6$ by $KClO_3Aq$ (Henry, *J. Ph.* 25, 265).

Thallium chlorate. By adding $TlNO_3Aq$ to $KClO_3Aq$; the solution is decomposed by heat and on evaporation $TClO_4$ separates out (Crookes, *C. N.* 8, 195). A *chlorate of ytterbium* was obtained by Popp (*A.* 131, 179).

IV. PERCHLORIC ACID AND PERCHLORATES. $HClO_4$; $MClO_4$. Mol. w. unknown for either the acid or its salts.

Stadion (*G. A.* 52, 197 a. 339) prepared potassium perchlorate by the action of H_2SO_4Aq on $KClO_3$; he obtained the acid by decomposing the new salt by H_2SO_4Aq. Serullas (*A. Ch.* [2] 45, 270; 46, 294 a. 323), prepared the same perchlorate by heating $KClO_3$ until the melted mass became semi-solid. The acid has been investigated by Roscoe (*A.* 121, 346).

Formation.—1. By heating $HClO_3Aq$, O and Cl being also evolved (Serullas, *l.c.*).—2. By the electrolysis of ClAq, or HClAq (Riche, *C. R.* 46, 348).—3. By electrolysis of $KClO_3Aq$, with Pt electrodes, ozone is evolved and $KClO_4$ and traces of KCl are formed (Lidoff a. Tichomiroff *J. R.* 1882. 341).—4. By adding ozone to HClOAq Fairly (*B. A.* 1874. 58).

Preparation.—1. $KClO_4$ is prepared by fusing $KClO_3$ until the liquid mass becomes pasty; $2KClO_3 = KClO_4 + KCl + O_2$. Marignac (*B. J.* 24, 192) says that when $6\frac{1}{2}$ litres O are evolved from 100 grams of $KClO_3$ the residue contains 65–66 p.c. $KClO_4$. The fused mass is repeatedly digested at 100° with conc. HClAq, to decompose $KClO_3$; the residue is dissolved in the smallest quantity of boiling H_2O; the crystals which separate on cooling are again digested with HClAq at 100°, and crystallisation is repeated from boiling water. Pure $KClO_4$ gives no yellow colour on digestion with conc. HClAq. One part $KClO_4$ is distilled with 4 parts very conc. pure H_2SO_4 so long as the distillate solidifies in the receiver; the crystalline distillate is melted, poured into a small retort, and gradually heated to 110° when yellowish fumes come off and a brownish-yellow distillate is formed. This distillate is redistilled very slowly and cautiously, heating being stopped whenever crystals begin to form in the neck of the retort. The distillate is preserved in small sealed glass bulbs.—2. 600 grams $KClO_3$ are boiled with the H_2SiF_6Aq prepared from 1000 grams CaF_2; after cooling, the K_2SiF_6 is filtered off; the solution of $HClO_3Aq$ is heated until white fumes of $HClO_4$ appear; the liquid is then slowly distilled from a retort; the distillate is freed from HClAq and H_2SO_4Aq by shaking with $AgClO_4$ and $Ba(ClO_4)_2$, filtered, and again distilled. From this $HClO_4Aq$, the pure acid may be obtained by distilling with 4 volumes conc. H_2SO_4, and rectifying as described in 1 (Roscoe, *A.* 121, 346).

The first product of the action of H_2SO_4 on $KClO_4$ is nearly pure $HClO_4$; this is succeeded by a liquid containing 72·4 p.c. $HClO_4$, when this drops into the receiver crystals of $HClO_4.H_2O$ are formed. When these crystals are slowly heated $HClO_4$ distils over, but after a time the liquid containing 72·4 p.c. $HClO_4$ is formed in the retort, and coming into contact with the $HClO_4$ forms crystals of $HClO_4.H_2O$.

Properties.—$HClO_4$ is a colourless, oily, volatile, liquid; S.G. 1·782 at 15°. Fumes strongly in moist air. Very easily undergoes decomposition with explosion, even when kept in glass bulbs in the dark. Cannot be distilled without decomposition; at 75° change begins; at 92° white clouds come off, and a yellow gas smelling like ClO_2, also a few drops of a liquid resembling Br; at a higher temperature violent explosion occurs; the residue solidifies to white crystals with 87·76 p.c. $HClO_4$ (Roscoe). $HClO_4$ is an extremely powerful oxidiser; one drop on charcoal, paper, wood, &c., produces combustion with violent explosions. A drop falling on to the skin produces a severe wound. When the hydrate $HClO_4.H_2O$ (*v. Combinations*, No. 1) is distilled under ordinary pressure nearly pure $HClO_4$ passes over at 110°. The temperature then rises until 203° is reached, when it becomes constant, and a heavy oily liquid, exactly resembling conc. H_2SO_4, distils over; the same liquid is obtained by distilling $HClO_4Aq$ until 203° is reached. This liquid contains 72·1 p.c. $HClO_4$, and does not correspond to a definite hydrate ($HClO_4.2H_2O = 73·6$, $HClO_4.3H_2O = 65·05$, p.c. H_2O) (Roscoe, *l.c.*; *v.* also Weppen, *A.* 29, 318).

Reactions and Combinations.—1. $HClO_4$ combines with water with a hissing sound and production of much heat; Berthelot gives $[HClO_4,Aq] = 20,300$ (*A. Ch.* [5] 27, 214). If water is added little by little, crystals of the hydrate $HClO_4.H_2O$ are obtained; these melt at about 50°; S.G. (liquid) 1·81 at 50°; decomposition into $HClO_4$ and $HClO_4.xH_2O$ begins at 110°.—2. $HClO_4Aq$ is not reduced by H_2S, SO_2, or HNO_2Aq, nor by any known substance according to Berthelot (*Bl.* [2] 38, 1). 3. $HClO_4Aq$ dissolves Zn and Fe with evolution of H.

Perchlorates.—$HClO_4$ is a monobasic acid forming one series of salts, $MClO_4$ or $M^{II}(ClO_4)_2$; a few basic salts are also known, *e.g.* $BiO.ClO_4$. These salts are prepared by the action of $HClO_4Aq$ on metals, oxides, or carbonates; or by the decomposition of $Ba(ClO_4)_2Aq$ by sulphates; or by the decomposition of chlorates by heat (*v.* POTASSIUM CHLORATE), or by H_2SO_4Aq, or by HNO_3Aq (Penny, *A.* 37, 203). The perchlorates are generally easily soluble in water; $KClO_4$ is one of the least soluble of the salts. They are isomorphous with the permanganates. They are decomposed by heat into chlorides and O, or into oxides, Cl, and O, but at higher temperatures than chlorates. When $KClO_3$ is heated so as to evolve only a part of its O, some $KClO_4$ is formed (Frankland a. Dingwall, *C. J.* 51, 278; Teed, *C. J.* 51, 283). Conc. H_2SO_4 forms $HClO_4$ at 100°; conc. HClAq does not act on perchlorates at 100°. Solutions of perchlorates are very slowly, if at all, reduced by reagents which readily reduce chlorates.

The following perchlorates have been prepared: $NH_4.ClO_4$ (Roscoe); isomorphous with $KClO_4$; $Ba(ClO_4)_2$ (Groth, *P.* 133, 226; Potilitzin, *C. C.* 1887. 1218); $Cd(ClO_4)_2$, very deliquescent (Serullas, *A. Ch.* [2] 45, 270; 46, 294 a. 323);

$Ca(ClO_4)_2$, very deliquescent (Serullas, *l.c.*); $Cu(ClO_4)_2$, large, blue, deliquescent crystals (Serullas, Roscoe); $Fe(ClO_4)_2$, long colourless needles, stable in air (Serullas); $Fe(ClO_4)_2.3H_2O$, greenish, very deliquescent, crystals (Roscoe); $Mn(ClO_4)_2$, deliquescent, not obtained in crystals (Serullas); $HgClO_4$, non-deliquescent needles (Serullas); $HgClO_4.1\frac{1}{2}H_2O$, very deliquescent (Roscoe); $Hg(ClO_4)_2$ (Serullas); $KClO_4$ (*v.* $HClO_4$, *Preparation*); S. (15°) 1·6, nearly insoluble in alcohol; $AgClO_4$ (Serullas); $NaClO_4$ (Penny, *A.* 37, 203); $TlClO_4$ decomposes in moist air (Crookes, *C. N.* 8, 195); $Zn(ClO_4)_2$ deliquescent needles. M. M. P. M.

CHLORINE, SULPHIDE OF, better called Sulphur chloride; *v.* SULPHUR.

CHLORITES — *Salts of Chlorous acid*, *v.* CHLORINE, OXY-ACIDS OF, p. 18.

CHLORO-. *Use of this prefix applied to inorganic compounds*; for *Chloro- compounds* and *Chloro- salts v.* the element the chloro- compound of which is sought for, or the salts to the names of which *Chloro-* is prefixed. Thus *Chloro-phosphide of nitrogen* will be found under NITROGEN, and *Chloro-platinate of potassium* under PLATINATES.

CHLORO-ACETAL *v.* CHLORO-ACETIC ALDEHYDE and CHLORAL.

CHLORO-ACETAMIDE *v.* CHLORO-ACETIC ACID, and ACETO-CHLORO-AMIDE, vol. i. p. 5.

CHLORO-ACETAMIDO- *v.* CHLORO-AMIDO-.

CHLORO-ACETANILIDE *v.* CHLORO-ANILINE.

ν-Chloro-acetanilide *v.* ANILINE, vol. i. p. 274.

CHLORO-ACETENE. Is merely a mixture of aldehyde, paraldehyde, and $COCl_2$ (Kekulé a. Zincke, *A.* 162, 141; *cf.* Harnitzky, *A.* 111, 192).

CHLORO-ACETIC ACID $C_2H_3ClO_2$ *i.e.* $CH_2Cl.CO_2H$. Mol. w. 94·5. [63°]. An unstable modification [52°] (Tollens, *B.* 17, 664). (186°). S.G. $\frac{73}{10}$ 1·366.

Formation.—1. From ethylene and chlorine peroxide (Fürst, *B.* 11, 2188; *A.* 206, 78).—2. Together with AcCl by the action of chlorine on acetic anhydride (Gal, *A.* 122, 374).—3. By passing chlorine into acetyl chloride mixed with iodine and decomposing the product with water (Jazukowitsch, *Z.* 1868, 234).—4. Chloro-acetyl chloride is formed, together with di-chloro-acetyl chloride, by boiling AcCl (40g.) with PCl_5 (200g.) for some weeks (Michael, *J. pr.* [2] 35, 95).

Preparation.—1. Dry chlorine is passed into a retort containing acetic anhydride heated to 100°, dry acetic acid being simultaneously run in. The acetyl chloride which is formed:

$$(CH_3.CO)_2O + Cl_2 = CH_2Cl.CO_2H + CH_3.CO.Cl$$

is at once reconverted by the acetic acid into anhydride, which is again attacked by the chlorine, and so on, so that a small quantity of anhydride suffices for the chlorination of a large quantity of acetic acid. When the absorption of the chlorine slackens the mixture is fractionally distilled (Hentschel, *B.* 17, 1286; *cf.* R. Hoffmann, *A.* 102, 1).—2. By passing chlorine through a heated mixture of 50 g. iodine and 500 c.c. nearly glacial acetic acid S.G. 1·065. The rectified product contains a little iodo-acetic acid (Hugo Müller, *C. J.* 17, 398).

Properties.—Deliquescent trimetric tablets or needles. Blisters the skin; nearly inodorous. V. sol. water, with absorption of heat.

Reactions.—1. *Water* slowly converts it on heating into glycollic acid (Buchanan, *B.* 4, 340, 863). *Caustic potash* acts similarly, while baryta forms di-glycollic acid $C_4H_6O_5$ (Kekulé, *A.* 105, 288; *cf.* Schwab, *R. T. C.* 2, 46).—2. Chloro-acetic acid (10 g.) boiled with PCl_5 (88 g.) yields tetra-chloro-ethylene and other bodies (Michael, *Am.* 9, 216).—3. *Sodium-amalgam* partially reduces it to acetic acid.—4. By heating with *dimethylaniline* it is broken up into methyl chloride and CO_2; this decomposition is produced by the intermediate formation of the body $PhMe_2ClN.CH_2.CO_2H$, which splits up into CO_2, CH_3Cl, and dimethylaniline (Silberstein, *B.* 17, 2661).

Salts.—KA′ 1½aq: laminæ, v. sol. water but not deliquescent and not dehydrated at 100°, but converted into glycollic acid at a higher temperature. The same change takes place when its aqueous solution is evaporated even below 100°.—KHA'_2: small pearly crystals, sl. sol. water.—BaA'_2aq: prisms. Decomposed but slightly when its aqueous solution is evaporated, and separates almost completely on cooling a hot saturated solution.—AgA′: pearly scales; detonates at 110°–120°.

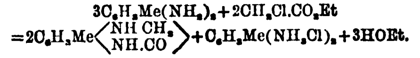
Methyl chloro-acetate $CH_2Cl.CO_2Me$ (130°) (Schreiner, *A.* 197, 1). V.D. 3·71 (for 3·74). S.G. $\frac{15}{}$ 1·22; $\frac{19}{}$ 1·235 (Henry, *C. R.* 101, 250). S.H. ·389 (R. Schiff, *G.* 17, 286). Prepared by passing HCl into a solution of chloro-acetic acid in MeOH (Henry, *B.* 6, 743) or from $CH_2Cl.CO.Cl$ and MeOH (P. J. Meyer, *B.* 8, 1152). Insol. water. Converted by ammonia into chloro-acetamide.

Chloro-methyl ether $CH_2Cl.CO_2.CH_2Cl$. (197°). S.G. $\frac{10\cdot6}{10\cdot6}$ 1·322. From $CH_2Cl.CO.Cl$ and glycolic chlorhydrin (Henry, *C. R.* 97, 1308).

Ethyl ether $CH_2Cl.CO_2Et$. Mol. w. 122½. V.D. 4·24 (calc. 4·23). (143°) (Schreiner, *A.* 197, 1); (144·5°) (Schiff, *A.* 220, 108). S.G. $\frac{20}{4}$ 1·1585 (Brühl, *A.* 203, 21). S.H. ·401. μ_β 1·428. R_∞ 43·51. S.V. 123·1.

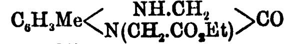
Formed by mixing chloro-acetyl chloride with alcohol in the cold (Willm, *A. Ch.* [3] 49, 97; *A.* 102, 109); or by heating chloro-acetic acid (200 g.) with alcohol (120 g.) and H_2SO_4 (25 g.) for 6 hours at 100° (Conrad, *A.* 188, 218). Oil with ethereal odour. With ammonia it forms chloro-acetamide. It unites with Me_2S at 100° forming the hydrochloride of di-methyl-thetine (Crum Brown a. Letts, *Pr. E.* 28, 583).

Chloro-acetic ether (2 mols.) heated with (1, 3, 4) tolylene-diamine (3 mols.) at 100° forms oxy-toluquinoxaline dihydride thus:



$$3C_6H_3Me(NH_2)_2 + 2CH_2Cl.CO_2Et$$
$$= 2C_6H_3Me\left\langle\begin{matrix}NH.CH_2\\NH.CO\end{matrix}\right\rangle + C_6H_3Me(NH_2Cl)_2 + 3HOEt.$$

When, however, chloro-acetic ether (2 mols.) is heated with a smaller quantity (1 mol.) of tolylene-diamine at 100° a compound $C_{13}H_{16}N_2O_3$ [147°] is formed; it may be



$$C_6H_3Me\left\langle\begin{matrix}NH.CH_2\\N(CH_2.CO_2Et)\end{matrix}\right\rangle CO$$

(Hinsberg, *A.* 237, 361).

Chloro-ethyl ether $CH_2Cl.CO_2.CH_2.CH_2Cl$. (198° uncor.). S.G. $\frac{10\cdot6}{}$ 1·322. From chloro-acetyl chloride and glycolic chlorhydrin (Henry, *C. R.* 97, 1308). Also from ethylene and Cl_2O (Mulder a. Bremer, *B.* 11, 1958).

Propyl ether $CH_2Cl.CO_2Pr$. (161°) (Schreiner, *A.* 197, 1). S.G. ^{0} 1·11 (Henry, *J. pr.* [2] 31, 127). S.H. ·422 (Schiff, *G.* 17, 486).

n-Butyl ether $CH_2Cl.CO_2C_4H_9$. (175°). S.G. ^{0} 1·103; ^{15} 1·081. V.D. 5·1 (Gehring, *Bl.* [2] 46, 146; *C. R.* 102, 1399).

Isoamyl ether $CH_2Cl.CO_2C_5H_{11}$. (190°). S.G. ^{0} 1·063 (Hugounenq, *Bl.* [2] 45, 328).

sec-Octyl ether $CH_2Cl.CO_2C_8H_{17}$. (234°). S.G. ^{10} ·990. From octyl alcohol of castor oil (Gehring, *C. R.* 104, 1000).

Phenyl ether $CH_2Cl.CO_2Ph$. [40°]. (230°–235°). From phenol and chloro-acetyl chloride. Needles (Prevost, *J. pr.* [2] 4, 379).

Benzyl ether CH_2PhA'. (148°) at 9 mm. S.G. $\frac{4}{4}$ 1·222.

Chloride v. CHLORO-ACETYL CHLORIDE.

Amide $CH_2Cl.CO.NH_2$. *Chloro-acetamide.* [119°] (Menschutkin a. Jermolajeff, *Z.* [2] 7, 5); [116°] (Bauer, *A.* 229, 165). (225°). S. 10 at 24°. S. (alcohol) 9·5 at 24°. From chloro-acetic ether and aqueous or gaseous NH_3, or from chloro-acetyl chloride and dry ammonia (Willm, *A. Ch.* [3] 49, 99). Thick monoclinic prisms or flat plates (from alcohol). Its aqueous solution after treatment with HgO deposits slender needles of $Hg(NH.CO.CH_2Cl)_2$. Alcoholic KCy forms $C_{14}H_{18}Cl_8N_4O_5$ (?) (Schiff a. Speciale, *G.* 9, 335). Br and KOHAq give chloro-methyl-chloro-acetyl-urea $CH_2Cl.NH.CO.NH.CO.CH_2Cl$. (Wallach, *A.* 184, 30).

Anilide $CH_2Cl.CO.NPhH$. [134°]. From aniline and ethereal $CH_2Cl.COCl$ (Wallach a. Kamensky, *A.* 214, 221; Tommasi, *Bl.* 19, 400; Cech, *B.* 10, 1376; Meyer, *B.* 8, 1152). Crystallises from benzene. When treated with PCl_5 it gives off HCl and forms a base whose hydrochloride is insol. water, benzene or ether, but crystallises from alcohol in long yellow silky needles which appear to be $C_{16}H_{12}Cl_2N_2HCl$.

p-Toluide $CH_2Cl.CONHC_6H_4Me$. [162°] (Meyer; Tommasi, *C. J.* 26, 911; 27, 628).

Nitrile $CH_2Cl.CN$. (124°). S.G. ^{20} 1·193. V.D. 2·62. From the amide and P_2O_5. The yield is 50 p.c. of the theoretical (Bisschopinck, *B.* 6, 732; Engler, *B.* 6, 1003; Bauer, *A.* 229, 165).

Di-chloro-acetic acid $C_2H_2Cl_2O_2$ *i.e.* $CHCl_2.CO_2H$. (190°). S.G. ^{15} 1·522.

Formation.—1. By the chlorination of acetic or of chloro-acetic acid (Maumené, *Bl.* [2] 1, 417). 2. By the action of aqueous KCy upon chloral (Wallach, *A.* 173, 295).

Preparation.—By boiling chloral hydrate (50 g.) with water (250 g.) and K_4FeCy_6 (84 g.); the resulting potassium salt being extracted by alcohol (Wallach, *B.* 9, 1212; 10, 1526).

Properties.—Corrosive liquid; solidifies below 0°.

Reactions.—1. Converted into glyoxylic acid by heating with moist Ag_2O. The same reaction is slowly effected by water at 100°, and by alkalis (Beckurts a. Otto, *B.* 14, 583).

Salts.—KA′: laminæ (from alcohol).—AgA′: prisms, sl. sol. cold water; decomposes violently at 80°.—CaA'_2 3aq: needles (from alcohol).—$Na(UrO)_2A'_3$ (Clarke a. Owens, *B.* 14, 35).

p-Toluidine di-chloro-acetate $C_6H_4Me.NH_3O.CO.CHCl_2$: [136°]; white needles (Duisberg, *B.* 18, 194).

Methyl ether $CHCl_2.CO_2Me$. (144°) (Wallach, *A.* 173, 299). S.G. ^{12} 1·381 (Henry, *C. R.* 101, 250). S.H. ·322 (Schiff, *G.* 17, 286).

Ethyl ether $CHCl_2.CO_2Et$. (157°). S.G. $\frac{20}{4}$ 1·2821 (Brühl, *A.* 203, 22). μ_β 1·444. R_∞ 52·19. V.D. 5·38 (for 5·42). S.H. ·338 (S.). S.V. 143·4. *Formation.*—1. Together with glyoxylic ether by heating C_2Cl_4 with NaOEt at 100°–150° for 13 hours.—2. By adding chloral hydrate (1 mol.) to potassium cyanide (1 mol.) in absolute alcohol:

$$CCl_3.CH(OH)_2 + EtOH + KCN$$
$$= CHCl_2.CO_2Et + HCN + KCl + H_2O.$$

Or by gently heating chloral cyanhydrin (1 mol.) with alcoholic NaOEt (Wallach, *B.* 6, 114; 10, 1527, 2120). *Reactions.*—1. Boiling alcoholic KCy gives acetic and oxalic acids (Claus, *B.* 11, 496, 1044).—2. *Silver*, or Na, converts it into maleic ether. 3. Alcoholic KOH gives glycollic acid (Claus, *B.* 14, 1066).

Propyl ether $CHCl_2.CO_2Pr$. S.H. ·352.

Isobutyl ether $CHCl_2.CO_2CH_2Pr$. (183°).

s-Octyl ether $CHCl_2.CO_2C_8H_{17}$. (214°) (Gehring, *C. R.* 104, 1000).

Benzyl ether $CHCl_2.CO_2.CH_2Ph$. (179°) at 60 mm. S.G. $\frac{4}{4}$ 1·313 (Seubert, *B.* 21, 281).

Amide $CHCl_2.CONH_2$. [98°] (Hantzsch a. Zeckendorff, *B.* 20, 1309). (234°). From the ether and alcoholic NH_3, or from chloral cyanhydrin $CCl_3.CH(OH).CN$ and aqueous NH_3 (Pinner a. Fuchs, *B.* 10, 1066). Monoclinic columns. V. sol. hot water. It unites with chloral forming $CCl_3.CH(OH).NH.CO.CHCl_2$, which crystallises from water in prisms. PCl_5 converts it into $CHCl_2.CCl:N.POCl_2$ (Wallach, *A.* 184, 28).

Ethylamide $CHCl_2.CONHEt$. [59°]. (226°). Converted by PCl_5 into $CHCl_2.CCl_2.NEt.POCl_2$ (140°–150°) and $CHCl_2.CCl:NEt$ (c. 163°).

Anilide $CHCl_2.CO.NHPh$. [118°]. *Formation.*—1. By the action of aniline on chloral in presence of KCy or on chloral cyanhydrin (Cech, *B.* 9, 337; 10, 1265).—2. From aniline, di-chloro-acetic acid, and P_2O_5 (C.).—3. By warming di-chloro-acetamide with aniline (C.). *Properties.* Crystalline scales (from water), sl. sol. hot water; sol. KOHAq and reppd. by acids.

Nitrile $CHCl_2.CN$. (113°). V.D. 3·82. S.G. ^{11} 1·374 (Bisschopinck, *B.* 6, 732). Formed by distilling the amide with P_2O_5. Absorbs HCl forming a crystalline compound which, when heated in a sealed tube at 140°, splits up into HCl and a *polymeride* of dichloro-acetonitrile [70°] (Weddige a. Körner, *J. pr.* [2] 31, 176).

Di-chloro-ortho-acetic ether $CHCl_2.C(OEt)_3$. (205°). Formed together with other bodies by heating C_2Cl_4 with NaOEt at 100°–120°. Decomposed by water. Decomposed by NaOEt into NaCl and di-ethyl-glyoxylic ether (Geuther a. Brockhoff, *J. pr.* [2] 7, 101).

Tri-chloro-acetic acid $C_2HCl_3O_2$ *i.e.* $CCl_3.CO_2H$. Mol. w. 163½. [55°]. (195°). S.G. $\frac{46}{15}$ 1·617. V.D. 5·3. *Formation.*—1. By the action of dry chlorine (3 mols.) on glacial acetic acid (1 mol.) in sunshine (Dumas, *A. Ch.* [2] 73, 75).—2. By the oxidation of chloral with HCl and $KClO_3$, and of chloral or metachloral with fuming HNO_3 (Kolbe, *A.* 54, 182).—3. Together with C_2Cl_6 by passing chlorine into C_2Cl_4 under water in sunlight (K.). 4. From $CCl_3.CO.Cl$, which is formed by chlorinating ether (Malaguti, *A. Ch.* [3] 16, 10).

Preparation. 1. Chloral hydrate (165½ pts.) is just melted and fuming HNO_3 (63 pts.) is added. The reaction proceeds without application of heat, and after half an hour the liquid is fractionally distilled (De Clermont, *A. Ch.* [6] 6, 135;

[5] 2, 401; *C. R.* 73, 112, 501; 74, 942; 76, 774; 81, 1270; *cf.* Tommasi a. Meldola, *C. J.* 27, 314; Judson, *Z.* [2] 7, 40).—2. Chloral hydrate (165 g.) is mixed with $KClO_3$ (37½ g.); as soon as the mixture is melted a violent action sets in, with evolution of gas, and potassium tri-chloro-acetate (120 g.) is formed (Seubert, *B.* 18, 3336, 3339).

Properties. — Deliquescent rhombohedral scales. V. sol. water. Blisters the skin. Its vapour is pungent. Markedly exhibits superfusion.

Reactions.—1. Conc. H_2SO_4 forms CO, CO_2, and HCl.—2. Both the acid and its salts are decomposed by boiling with *water* or *alkalis* into CO_2 and chloroform. *Ammonia*, *dimethylaniline*, and KCy also liberate chloroform (Silberstein, *B.* 17, 2664; Bourgoin, *Bl.* 37, 403; *C. R.* 94, 448).—3. It is *reduced* to acetic acid by fuming HI at 100° (Clermont), by electrolysis (K.), or, in aqueous solution, by (⅔ p.c.) potassium amalgam (Melsens, *A. Ch.* [3] 10, 233).—4. NaOEt forms sodium chloride, carbonate, and formate.—5. K_2SO_3Aq for $CHCl(SO_3K)CO_2K\,1\frac{1}{2}aq$ (Rathke, *A.* 161, 149).—6. Forms a compound with *aluminum chloride* which is decomposed by steam thus: $(CCl_3.CO_2)_2Al_2Cl_4 + 6H_2O = 2CHCl_3 + 2CO_2 + 4HCl + Al_2(OH)_6$ (Elbs a. Tolle, *J. pr.* [2] 32, 624).

Salts.—KA′aq: long slender needles. Heated with bromine it forms CO_2, KBr, and $CBrCl_3$ (Van 't Hoff, *B.* 10, 678).—KHA'_2: octahedra. S. 26·1 at 0°; 33·75 at 20° (Seubert).—NaA′ 3aq. On dry distillation it gives NaCl, CO, CO_2, $COCl_2$, tri-chloro-acetyl chloride, tri-chloro-acetic acid and its anhydride, and a little C_2Cl_6 (Henry, *B.* 12, 1844).—NH_4A' 2aq: [80°]; prisms. Boils at 110°–115°, giving off chloroform and ammonium bi-carbonate, and leaving NH_4A', which is solid at 160°, but at a higher temperature splits up into NH_4Cl, CO, and $COCl_2$ (M.).—$NH_4HA'_2$: octahedra—LiA′2aq: deliquescent prisms—TlA′—$TlHA'_2$—AgA′: laminæ, sl. sol. water; explodes when heated, forming AgCl, CO, CO_2, and tri-chloro-acetic anhydride. —$CaA'_2$6aq: prismatic needles. —$CaA'_2$3½aq.—$SrA'_2$6aq: radiate groups of prisms.—$BaA'_2$6aq: very thin laminæ. — MgA'_2 4aq.—ZnA'_2 6aq: laminæ.—$CuA'_2$6aq (Judson, *B.* 3, 782).—HgA'_2: prismatic needles.—$Hg_2A'_2$: small needles, sl. sol. water.—PbA'_2aq: large prisms, v. sol. water, sl. sol. alcohol.

Methyl ether $CCl_3.CO_2Me$. (154°) (Henry, *C. R.* 101, 250). S.G. $\frac{19}{}$ 1·489. S.H. ·277 (Schiff, *G.* 17, 286). Obtained by distilling the acid with methyl alcohol and H_2SO_4; or by the action of methyl alcohol on the chloride or chlorinated aldehyde. Oil, smelling of peppermint.

Tri-chloro-methyl ether $CCl_3.CO.OCCl_3$. S.G. $\frac{18}{}$ 1·705. (c. 200°). From the preceding or from methyl acetate by chlorine in sunshine. Said to be identical with the penta-chloro-ethyl ether of chloro-formic acid $Cl.CO.O.CCl_2.CCl_3$, (180°–185°), S.G. $\frac{10}{}$ 1·724 (Cahours, *A.* 64, 315). Decomposed by moist air and by aqueous alkalis into HCl, CO_2, and tri-chloro-acetic acid. *Reactions.*—1. *Ammonia* gives tri-chloro-acetamide.—2. *Alcohol* gives tri-chloro-acetic ether and chloroformic ether; methyl alcohol acts similarly.—3. Its vapour passed through a *red-hot tube* gives $COCl_2$ and tri-chloro-acetyl chloride.

Ethyl ether $CCl_3.CO_2Et$. (167°). S.G. $\frac{20}{4}$ 1·3826 (Brühl). μ_β 1·4567. R_∞ 60·57. S.H. ·296. V.D. 6·59 (for 6·61). S.V. 163·8 (Schiff). Obtained by distilling the acid with alcohol and a little H_2SO_4 (Clermont, *A. Ch.* [6] 6, 241). Oil, smelling of peppermint. Heated with KCy and absolute alcohol it yields CO_2 and chloroform (Claus, *A.* 191, 58). PCl_5 at 150° forms EtCl, $POCl_3$, and $CCl_3.COCl$ (Michael, *Am.* 9, 213). Heated with NaOEt (containing NaOH) it forms orthoformic ether, NaCl, and $NaEtCO_3$ (Klien, *J.* 1876, 521). With K_2SO_3 it forms $CHCl(SO_3K)_2CO_2K\,1\frac{1}{2}aq$ (Rathke, *A.* 161, 166).

Penta-chloro-ethyl ether $CCl_3.CO_2C_2Cl_5$. (245°). S.G. $\frac{25}{}$ 1·79 (Malaguti, *A. Ch.* [3] 16, 57; Cloez, *A. Ch.* [3] 17, 304). Formed by passing chlorine through acetic ether, finally in sunshine (Leblanc, *A. Ch.* [3] 10, 200). Liquid, gradually decomposed by moist air into HCl and tri-chloro-acetic acid *Reactions.*—1. *Alcohol* forms tri-chloro-acetic ether.—2. *Ammonia* forms tri-chloro-acetamide. 3. Prolonged action of *chlorine* forms C_2Cl_6.—4. Passage through a tube at 400° yields tri-chloro-acetyl chloride.

Propyl ether $CCl_3.CO_2Pr$. (187°) (Clermont, *C. R.* 96, 437). S.H. ·306.

Isobutyl ether $CCl_3.CO_2.CH_2Pr$. (188°) (J.).

Isoamyl ether $CCl_3.CO_2C_5H_{11}$. (217°) (C.).

s-Octyl ether $CCl_3.CO_2C_8H_{17}$. (260°) (Gehring, *C. R.* 104, 1001). Light oil.

Benzyl ether CH_2PhA'. (179°) at 50° mm. S.G. $\frac{4}{4}$ 1·389.

Anhydride $(CCl_3.CO)_2O$. (224°). Formed by treating the acid with PCl_3 or $CCl_3.COCl$ (Buckney a. Thomson, *B.* 10, 698; Clermont, *Bl.* [2] 30, 505; *C. R.* 86, 337). Hygroscopic liquid, rapidly converted into the acid by water.

Chloride v. Tri-CHLORO-ACETYL CHLORIDE.

Amide $CCl_3.CO.NH_2$. Mol. w. 162½. [136°]. (239°). Formed by the action of ammonia on tri-chloro-acetyl chloride, on tri-chloro-acetic ether, on perchlorinated acetic ether (*v. supra*), and on perchlorinated formic, carbonic, oxalic, and succinic ethers (Malaguti, *A.* 56, 286; Cloez, *A.* 60, 261, *A. Ch.* [3] 19, 352; Gerhardt, *Compt. Chim.* 1848, 277). *Preparation.*—By mixing NH_3 (1 pt.) dissolved in alcohol (10 pts.) with trichloracetic ether (11 pts.) dissolved in alcohol (16 pts.) The mixture is kept cool. After 12 hours the reaction is complete (A. Weddige, *J. pr* [2] 33, 78). *Properties.*—Monoclinic tables (from water); sweetish taste. Sl. sol. water, v. sol. alcohol and ether. *Reactions.*—1. *Ammonia* forms ammonium tri-chloro-acetate. —2. P_2O_5 gives the nitrile.—3. PCl_5 gives $CCl_3.CCl{:}N.POCl_2$ [c. 81°] (c. 257°) (Wallach, *A.* 184, 23).

Chloro-amide $CCl_3.CO.NHCl$. [121°]. Formed by the action of chlorine-water on tri-chloracetamide (Cloez, *A. Ch.* [3] 17, 305). Very volatile with steam. Large plates. Sol. alcohol, and ether, sl. sol. water. It dissolves in NH_3Aq with re-formation of tri-chlor-acetamide. It is scarcely altered by boiling with alcoholic KOH. By neutralising the alcoholic solution of the chloro-amide with alcoholic KOH a well crystallised potassium salt ($CCl_3.CO.NClK$) is formed (Steiner, *B.* 15, 1606).

Methylamide $CCl_3.CONHMe$. [106°]. From tri-chloro-acetic ether and methylamine. Crystals, sl. sol. water and ether, slowly attacked by HNO_3 (Franchimont a. Klobbie, *R. T. C.* 6, 234).

Di-methyl-amide $CCl_3.CONMe_2$. [c. 12°].

(233°). S.G. ^{15} 1·441. V.D. 6·68. Not attacked by HNO_3 (S.G. 1·53) (F. a. K.).

Ethyl-amide $CCl_3.CO.NHEt$. [74°]. (230°). Quadrangular tables. Insol. cold water, v. sol. alcohol, ether, or chloroform (Wallach a. Kamensky, *A.* 214, 225). PCl_5 appears to form the imido-chloride $CCl_3CCl:NEt$, but this gives no basic condensation product.

Di-ethyl-amide $CCl_3.CONEt_2$. [27°]. (F. a. K.); [90°] (Cloez). V.D. 7·23 (F. a. K.). From hexa-chloro-acetone and NEt_2H (Cloez, jun., *A. Ch.* [6] 9, 145). Crystals. Not attacked by pure HNO_3 (S.G. 1·53) (F. a. K).

Allyl-amide $CCl_3.CO.NHC_3H_5$. [45°]. (190°). From allylamine and hexa-chloro-acetone (Cloez).

Anilide $CCl_3.CO.NPhH$. [94°]. Scales (from alcohol); gives no basic condensation product with PCl_5.

o-Toluide $CCl_3.CO.NH.C_6H_4Me$. [67°]. (215°). From hexa chloro-acetone and *o*-toluidine (Cloez, jun., *A. Ch.* [6] 9, 145).

p-Toluide $CCl_3.CO.NH.C_6H_4Me$. [80°]. (185°) (Cloez).

Nitrile $CCl_3.CN$. (84°). S.G. ^{12} 1·439. V.D. 5·03. Formed by the action of chlorine on acetonitrile containing iodine (Beckurts, *B.* 9, 1594). From the amide and P_2O_5; the yield is 90 p.c. (Dumas, Malaguti, a. Leblanc, *C. R.* 25, 442; Bisschopinck, *B.* 6, 732; Bauer, *A.* 229, 165). Pungent liquid, insol. water, sol. alcohol, ether, and light petroleum. Forms a crystalline compound with HBr which is decomposed by water. Warmed with HCl changes to trichloro-acetic acid. Polymerises when kept. NaOEt forms ethyl derivatives of the nitriles of dichloro-glycollic acid, and of chloro-glyoxylic acid.

Paranitrile $(CCl_3.CN)_3$. *Per-chloro-tri-methyl-cyanidine.* [96°]. *Formation.*—1. Cyanoformic ether, $CN.CO_2Et$, is distilled with PCl_5, and the liquid product, probably CN.COCl, is heated in a sealed tube at 160° with PCl_5. The product is distilled with steam and crystallised from alcohol. The yield is 6 per cent. (A. Weddige, *J. pr.* [2] 28, 188; 33, 77).—2. From ordinary tri-chloro-acetonitrile by saturating it with HCl and exposing it, in sealed tubes, to sunlight. In about a year the contents of the tubes solidifies. The solid nitrile is crystallised from alcohol. *Properties.* Large prisms (from hot alcohol). Sol. alcohol, benzene, ether, CS_2, and chloroform. Hardly sol water. Volatile with steam. *Reactions.*—1. Decomposed by *alcoholic potash*, thus:

$$(CCl_3.CN)_3 + 3KOH = C_3N_3(OK)_3 + 3CHCl_3,$$

forming chloroform and potassic cyanurate.—2. Boiled with alcoholic *ammonia* it reacts thus:

$$C_3N_3(CCl_3)_3 + NH_3 = HCCl_3 + C_3N_3(CCl_3)_2.NH_2.$$

The latter body forms flat prisms (from alcohol) [166°]. It is sol. alcohol, ether, and benzene, scarcely sol. water. It is not a base.—3. When heated with alcoholic NH_3 in sealed tubes at 110° tri-chloro-acetic paranitrile reacts thus:

$$C_3N_3(CCl_3)_3 + 2NH_3 = 2CHCl_3 + C_3N_3(CCl_3)(NH_2)_2$$

The diamide crystallises from alcohol either in long pyramids containing alcohol or in short six-sided prisms without alcohol of crystallisation. It melts at [236°]. It is sl. sol. ether and benzene, hardly sol. cold water. It forms a salt, $C_3N_3(CCl_3)(NH_2)_2HCl$ 2aq., crystallising in pearly plates. This salt is decomposed by boiling water. Boiled with NH_3Aq it forms ammeline, or an isomeride $C_3N_3(OH)(NH_2)_2$.—4. Heated with NH_3Aq at 120°, or alcoholic NH_3 at 170° it forms $C_3N_3(OH)(NH_2)_2$ *v.* AMMELINE.—5. Aqueous or alcoholic *methylamine* at 20° forms $C_3N_3(CCl_3)_2NHMe$. Small crystals [117°]. V. sol. alcohol, sol. benzene. Is not a base. With alcoholic ammonia at 110° it gives rise to $C_3N_3(CCl_3)(NH_2)(NHMe)$. This body is also got from $C_3N_3(CCl_3)_2(NH_2)$ and alcoholic methylamine. It forms colourless crystals [153°–155°]. 6. Alcoholic methylamine at 110° in a sealed tube forms $C_3N_3(CCl_3)(NHMe)_2$. Small white crystals [207°]. Sol. alcohol and benzene. Forms salts.—7. Aqueous *methylamine* at 120° forms $C_3N_3(OH)(NMeH)_2$. Slender needles. Forms a platino-chloride $(B'HCl)_2PtCl_4$ (Weddige; *v.* also Hofmann, *B.* 18, 2770).

CHLORO-ACETIC ALDEHYDE $CH_2Cl.CHO$. (85°).

Formation.—1. From vinyl chloride, HClO, and HgO (Glinsky, *Z.* 1867, 678; 1868, 617; 1870, 647).—2. From di-chloro-ether and conc. H_2SO_4 (Jacobsen, *B.* 4, 216).

Preparation.—A mixture of chloro-acetal (1000 g.) and dry oxalic acid (590 g.) is distilled at 100°-150° in an atmosphere of CO_2. The residue consists chiefly of oxalic ether, the distillate contains formic ether, oxalic acid, and chloro-acetic aldehyde. A portion (87°-91°) purified by fractional distillation is obtained in the form of a crystalline hydrate either by use of a freezing mixture or by means of $NaHSO_3$. Water of crystallisation is removed by distillation over $CaCl_2$ or $CuSO_4$. The anhydrous aldehyde is, however, best obtained by distilling its polymeride (Natterer, *M.* 3, 442).

Properties.—Colourless liquid which combines with water, forming a crystalline hydrate, $CH_2Cl.CHO\ \frac{1}{2}aq$ [43°–50°]. The V.D. (1·98) of the hydrate shows that it dissociates. It forms monoclinic crystals. Sol. water, alcohol, and ether; blisters the skin. Reduces ammoniacal $AgNO_3$, forming a mirror.

Reactions.—1. *Oxidised* by HNO_3 to chloro-acetic acid. 2. *Potassium cyanide* gives an oil $(CH_2Cl.CHO)(CH_2Cy.CHO)$ whence HCl forms acetic and chloro-oxy-propionic acids.—3. By *heating* alone or with some H_2SO_4 it is converted into $\alpha\gamma$-di-chloro-crotonic aldehyde.—4. HCl passed into a mixture of chloro-acetic aldehyde and alcohol forms di-chloro-ether.

Combinations.—1. With *alcohol* it forms an alcoholate, $CH_2Cl.CH(OH)(OEt)$. (c. 94°). Also formed from di-chloro-ether with water (7 vols.) at 120° (Abeljanz, *A.* 1[illegible], 217). Repeated distillation converts it into $C_8H_{16}Cl_2O_3$ (164°).—2. With *acetyl chloride*: $CH_2Cl.CHCl(OAc)$. (c. 147°). Formed also by reducing the corresponding compound of chloral with acetyl chloride by Zn and acetic acid (Curie a. Millet, *B.* 9, 1611).—3. With *bisulphite of soda*: $C_2H_3ClONaHSO_3 2aq$: six-sided tables (from water). Separates from alcohol as a powder (containing $\frac{1}{2}$aq). Boiling Na_2CO_3 decomposes it without regenerating the chloro-acetic aldehyde.—4. With *calomel*: $C_2H_3ClOHg_2Cl_2$.

Chloro-acetic paraldehyde $(C_2H_3ClO)_3$. [87°]. (140°) at 10 mm. S.G. 2·77. V.D. 8·25 (calc. 8·31) An amorphous porcelain-like mass into which the aldehyde slowly changes on keeping (probably when not perfectly pure). It also separates from a solution of the hydrate in conc. H_2SO_4. Trimetric crystals, $a:b:c = 1·51:1:·941$. Insol. water, sl. sol. cold alcohol, v. sol. ether. At 245° it is reconverted into the ordinary modification. Not acted upon by iron and acetic acid, by AgOAc and HOAc, by alcoholic NH_3, by KOHAq at 100°, or by cold NaOEt (Natterer, *M.* 6, 519).

Chloro-acetic orthaldehyde $CH_2Cl.CH(OH)_2$. Contrary to analogy, the hydrate of chloro-acetic aldehyde does not seem to have the above formula, but appears to be $CH_2Cl.CH(OH).O.CH(OH).CH_2Cl$ (*v. supra*). The di-alkylated derivatives of chloro-acetic ortho-aldehyde are called acetals.

Ethyl ether $CH_2Cl.CH(OH)(OEt)$. *Chloro-aldehyde alcoholate.* (93°–95°). Formed by the action of water at 120° on dichlorinated ethyl oxide $CH_2Cl.CHCl.OEt$. On distillation it forms an anhydride, $(CH_2Cl.CH.OEt)_2O$, (163°–165°), which is split up by conc. H_2SO_4 into chloro-acetic aldehyde and alcohol. This body is also formed from di-chloro-di-ethyl ether and potash.

Acetyl derivative of the ethyl ether $CH_2Cl.CH(OEt)(OAc)$. (170°). From di-chloro-ethyl ether and silver acetate (Bauer, *A.* 134, 176).

Methyl ethyl ether $CH_2Cl.CH(OEt)(OMe)$. (137°). S.G. ^{11} 1·056. From di-chloro-ethyl ether and sodium methylate (Lieben, *A.* 146, 202).

Di-ethyl ether $CH_2Cl.CH(OEt)_2$. *Chloro-acetal.* (157°). S.G. ^{0} 1·042. V.D. 5·38 (calc. 5·29). *Formation.*—1. When chlorine is passed into dilute alcohol (80 p.c.) for some time, on adding water a heavy oil separates. By fractional distillation this is found to consist chiefly of aldehyde, chloro-acetal, and di-chloro-acetal. The fraction 120°–170° is digested for several days with aqueous KOH and rectified (Lieben, *A. Ch.* [3] 56, 313; Krey, *Jena. Zeit.* 10, 84). - 2. From di-chloro-ethyl ether $CH_2Cl.CHCl.OEt$ and NaOEt (Lieben, *A.* 146, 193; Natterer, *M.* 3, 444); or by long boiling with alcohol (Paterno a. Mazzara, *B.* 6, 1202).—3. From di-chloro-ethylene and alcoholic NaOEt at 40°-50° (Klien, *J.* 1876, 336).—4. By warming chloro-acetic aldehyde with alcohol (Natterer, *M.* 5, 497). *Properties.*—Aromatic liquid, insol. water, sol. alcohol. Not attacked by aqueous KOH. Does not pp. $AgNO_3$. — *Reactions.* — 1. NaOEt at 150° gives $CH_2(OEt).CH(OEt)_2$. — 2. *Sodium* forms $CH_2:CH.OEt$ (Wislicenus, *A.* 192, 106). -3. Boiling with powdered *zinc* gives EtCl and alcohol.—4. Heating with *oxalic acid* gives chloro-acetic aldehyde and oxalic ether. HOAc acts similarly.—5. HCl gives di-chloro-ethyl ether $CH_2Cl.CHCl.OEt$.—6. Poured upon *bleaching-powder*, no action ensues, but upon heating over a water bath a reaction takes place and a greenish liquid collects in the receiver. This distillate presently decomposes, the products being chlorine, HCl, undecomposed chloro-acetal, di- and tri-chloro-acetals, chloroform, and an aldehyde (Goldberg, *J. pr.* 132, 109).

Di-chloro-acetic aldehyde, $CHCl_2.CHO$. Mol. w. 113. (89°).

Formation.—1. By distilling di-chloro-acetal with H_2SO_4 (Grimaux a Adam, *Bl.* 34, 29; Paterno, *Z.* 1868, 667).—2. By boiling $CCl_2:CH.OMe$ with dilute H_2SO_4 (Denaro, *G.* 14, 119).—3. By distilling its hydrate obtained by chlorination of chloro-acetic paraldehyde (*v. di-chloro-acetic ortho-aldehyde*) with H_2SO_4.

Properties.—Liquid, which, in presence of some HCl, gradually changes to an amorphous solid variety, which at 120° returns to the liquid form.

Reactions.—1. *Oxidised* by HNO_3 to dichloro-acetic acid.—2. PCl_5 forms $CHCl_2.CHCl_2$ (147°) (Paterno, *Z.* 1868, 667).

Di-chloro-acetic paraldehyde $(CHCl_2.CHO)_x$. [130°]. S.G. 1·69. From di-chloro-acetic aldehyde (or di-chloro-acetal) in presence of H_2SO_4 in the cold (Jacobsen, *B.* 8, 87; *cf.* Krey, *J.* 1876, 475). Hexagonal pyramids (from alcohol). V. sol. hot alcohol. May be sublimed, but at 240° in a sealed tube, or with conc. H_2SO_4 at 130°, it changes to liquid di-chloro-acetic aldehyde.

Amorphous polymeride $(CHCl_2.CHO)_n$. Formed spontaneously by the polymerisation of (impure ?) di-chloro-acetic aldehyde (Friedrich, *A.* 206, 252). Paraffin-like mass, insol. water, m. sol. ether, sl. sol. hot alcohol. Does not melt below 200°. Converted by heat into ordinary di-chloro-acetic aldehyde.

Di-chloro-acetic orthaldehyde $CHCl_2.CH(OH)_2$. *Di-chloro-acetic aldehyde hydrate.* [43°] (F.); [57°] (Denaro, *G.* 14, 120) (c. 120°). Formed as a by-product in the preparation of tri-chloro-butyric aldehyde by the action of chlorine upon paraldehyde (Friedrich, *A.* 206, 251). Micaceous scales. V. sol. water and ether. Oxidised by HNO_3 to di-chloro-acetic acid. Conc. H_2SO_4 converts it into di-chloro-acetic aldehyde and its amorphous polymeride.

Di-ethyl ether $CHCl_2.CH(OEt)_2$. *Di-chloro-acetal.* Mol. w. 187. (184°). V.D. 6·45 (calc. 6·44). S.G. ^{14} 1·138. Formed by chlorinating alcohol (*v. supra*) or acetal (Lieben, *A.* 104, 114; Pinner, *B.* 5, 148; Krey, *J.* 1876, 474). Also from tri-chloro-ethyl ether $CHCl_2.CHCl.OEt$ and NaOEt (Jacobsen, *B.* 4, 217).

Reactions.—1. *Zinc-ethyl* at 140° gives propylene, ethylene, and other gases, leaving ether: (Paterno, *C. R.* 77, 458).—2. PCl_5 gives tri-chloro-ethyl ether $CHCl_2.CHCl.OEt$.—3. NaOEt gives the tetra-ethyl derivative of ortho-glyoxal $CH(OEt)_2.CH(OEt)_2$ (Pinner, *B.* 5, 151).—4. Conc. H_2SO_4 or HClAq converts it into di-chloro-acetic aldehyde. Fuming H_2SO_4 forms a crystalline compound $C_8H_7Cl_3O$, [129°] (Grabowsky, *B.* 6, 1071). According to Pinner (*A.* 179, 34) di-chloro-acetal is *not* converted into di-chloro-acetic aldehyde by H_2SO_4, and does *not* give di-chloro-acetic acid on oxidation by HNO_3.

Tri-chloro-acetic aldehyde *v.* Chloral.

Tri-chloro-acetic orthaldehyde *v.* Chloral *hydrate.*

Di-ethyl ether $CCl_3.CH(OEt)_2$ (*v.* p. 4).

An *isomeride*, possibly having the constitution $CHCl_2.CCl(OEt)_2$, [72°] (P.); [83°] (K.), (230°), is formed as a secondary product in the preparation of di-chloro-acetal by the chlorination of 80 p.c. alcohol (Paterno, *C. R.* 67, 765; Lieben, *A.* 104, 114; Kley, *J.* 1876, 475). Needles (from ether). Volatile with steam. It is doubtful whether it yields chloral on treatment with H_2SO_4; such a reaction would indicate the same formula as that ascribed to the liquid isomeride (*v.* p. 4).

TRI-CHLORO-ACETIC ANHYDRIDE *v. Anhydride* of *Tri*-CHLORO-ACETIC ACID.

CHLORO-ACETO-ACETIC ETHER $C_6H_9ClO_3$ *i.e.* $CH_3.CO.CHCl.CO_2Et$ or $CH_2Cl.CO.CH_2.CO_2Et$. (194°). S.G. ^{14} 1·19 Formed, together with SO_2 and HCl, by the action of SO_2Cl_2 (1 mol.) or of Cl upon aceto-acetic ether (1 mol.) (Allihn, *B.* 11, 568; Merves, *A.* 245, 58). Liquid. Alcoholic KOH liberates chloro-acetic acid. (*α*)-Naphthylamine forms $C_{16}H_{16}NO_2Cl$ [75°] (Bender, *B.* 20, 2747). Fuming HNO_3 forms chloro-nitroso-aceto-acetic ether $CH_3.CO.CCl(NO).CO_2Et$ (?) (Propper, *A.* 222, 48). Phenyl-hydrazine in ethereal solution forms $C_{12}H_{14}N_2O_2$ [51°], which is probably $CH_3.C(N_2Ph):CH.CO_2Et$, which may be reduced to oxy-phenyl-methyl-pyrazole.

Metallic compounds.—Formed as precipitates by shaking the ether with ammoniacal solutions of the metallic salts.—$(C_6H_8O_3Cl)_2Cu$: green leaflets.—$(C_6H_8O_3Cl)_2Mg$: white needles.—$(C_6H_8O_3Cl)_2Ni$: light-green powder—$(C_6H_8O_3Cl)_2Co$: light-red powder (Hensgen, *B.* 12, 1300).—$C_6H_8O_3ClNa$: crystalline powder, v. sol. alcohol (Conrad a. Guthzeit, *B.* 16, 1551).

Di-chloro-aceto-acetic ether $CH_3.CO.CCl_2.CO_2Et$ or $CHCl_2.CO.CH_2.CO_2Et$. (206°). S.G. $\frac{16}{17.5}$ 1·293. Formed, together with SO_2 and HCl, by the action of SO_2Cl_2 (2 mols.) on aceto-acetic ether (1 mol.) (Allihn, *B.* 11, 567). Formed also by chlorinating aceto-acetic ether (Conrad, *A.* 186, 232). Liquid. Decomposed by dilute HCl at 180° into CO_2, alcohol, and di-chloro-acetone. KOH gives di-chloro-acetic and acetic acids. Decomposed by KCN into HCN, acetic ether, and potassium di-chloro-acetate (James, *A.* 240, 65; *C. J.* 51, 287). Di-chloro-aceto-acetic acid does not form metallic salts, nor does it react with aldehydes (difference from di-bromo-aceto-acetic ether).

Tri-chloro-aceto-acetic ether $C_6H_7Cl_3O_3$ (223°). From aceto-acetic ether and Cl in daylight (Merves, *A.* 245, 70). With NaOEt it gives di-chloro-acetic ether.

CHLORO-ACETOL *v.* DI-CHLORO-PROPANE.

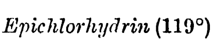
CHLORO-ACETONE C_3H_5ClO *i.e.* $CH_3.CO.CH_2Cl$. (118°). S.G. ^{13} 1·158 (Cloez).

Formation.—1. By electrolysis of a mixture of acetone and HCl (Riche, *C. R.* 49, 176).—2. From acetone and HClO (Mulder, *B.* 5, 1007). 3. By passing chlorine (1 mol.) into well-cooled acetone (M.).—4. By dissolving di-chloro-propylene $CH_2Cl.CCl:CH_2$ in conc. H_2SO_4 and distilling the product with water (Henry, *B.* 5, 190, 965).—5. From bromo- or chloro-propylene by the action of hypochlorous acid and HgO (Linnemann, *A.* 138, 122).—6. By oxidation of propylene chlorhydrin (from propylene glycol) with $K_2Cr_2O_7$ and H_2SO_4 (Morley a. Green, *B.* 18, 24).

Preparation.—By passing chlorine into acetone at 15° (Cloez, *A. Ch.* [6] 9, 145).

Properties.—Pungent oil; v. sl. sol. water. According to Cloez it is not pungent when quite pure, and the pungency can be removed by washing with very weak alkali. Volatile with steam. It gives a splendid crimson colour with solid KOH, or a strong aqueous solution of KOH. With $NaHSO_3$ it forms crystalline $C_3H_5Cl(OH)(SO_3Na)$ (Barbaglia, *B.* 6, 321).

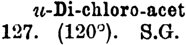
Reactions.—1. Zn and HCl reduce it to acetone.—2. Moist Ag_2O *oxidises* it to glycollic, acetic, and formic acids.—3. K_2SO_3 gives $CH_3.CO.CH_2.SO_3K$.—4. Potassium acetate forms $CH_3.CO.CH_2.OAc$.—5. Alcoholic KCN produces $CH_3.CO.CH_2CN$.—6. Fuming HNO_3 forms crystalline nitroso-chloro-acetone $C_3H_4ClNO_2$ [110°] (Glutz, *J. pr.* [2] 1, 141).—7. Alcoholic *ammonium sulphocyanide* gives the crystalline sulphocyanide [114°] of imido-propyl sulphocyanide $CH_3.C(NH).CH_2.SCN$ [42°] (Norton a. Tcherniak, *Bl.* [2] 33, 203).—8. *Barium sulphocyanide* forms $CH_3.CO.CH_2SCN$ which is an oil (Tcherniak a. Hellon, *B.* 16, 349).—9. *Bromine* at 100° forms chloro-tri-bromo-acetone.—10. *Ammonia* forms a compound ($CH_3.CO.CH_2NH_2$?) which gives methylamine on distillation with potash (Cloez). 11. Chloro-acetone (2 mols.) added to an aqueous solution of (1, 3, 4)-tolylene-diamine at 60° forms methyl-toluquinoxaline



$$C_6H_3Me\left\langle\begin{array}{l}N:CH\\ \quad|\\ N:CMe\end{array}\right.$$

[54°] (Hinsberg, *A.* 237, 368).—12. Alcoholic KOBz forms $CH_3.CO.CH_2.OBz$ (245° at 380mm.) (van Romburgh, *R. T. C.* 1, 53). 13. Conc. HCNAq forms the **cyanhydrin** $CH_3.C(OH)(CN).CH_2Cl$ which is the nitrile of chloro-oxy-isobutyric acid (chloro-acetonic acid) (C. Bischoff, *B.* 5, 865).

Isomeride of chloro-acetone C_3H_5ClO *i.e.*



$$CH_2Cl.\overset{\overbrace{\quad O \quad}}{CH.CH_2}$$

(?) *Epichlorhydrin* (119°). S.G. ^{11} 1·194 Obtained from glycerin dichlorhydrin $CH_2Cl.CH(OH).CH_2Cl$ and warm conc. KOH (Prevost, *P.* [2] 12, 160). Liquid. Combines with HCl, water, and HOAc forming derivatives of di-chlorhydrin. With alcoholic NH_3 it forms $C_3H_{12}ClNO_2$ (Cloez, *A. Ch.* [6] 9, 145).

u-**Di-chloro-acetone** $CHCl_2.CO.CH_3$. **Mol. w.** 127. (120°). S.G. ^{15} 1·234.

Formation.—By heating di-chloro-aceto-acetic ether with water at 180° (Conrad, *A.* 186, 235) or by boiling it with HClAq for 5 hours (V. Meyer, *B.* 15, 1165).

Preparation.—By the prolonged action of chlorine upon well-cooled acetone (Fittig, *A.* 110, 40; 133, 112; Mulder, *B.* 5, 1007; Cloez, *A. Ch.* [6] 9, 145).

Properties.—Pungent liquid, sl. sol. water. Combines with bisulphite of soda forming $C_3H_4Cl_2(OH)(SO_3Na)3aq$.

Reactions.—1. *Ammonia* forms the compound $CH_3.CO.CHCl(NH_2)$ which yields methylamine when distilled with potash.—2. PCl_5 gives tetra-chloro-propylene and a small quantity of penta-chloro-propylene.—3. KHS gives a yellow viscid body C_3H_4SO, the alcoholic solution of which gives with lead acetate a red pp. $C_3H_4SOPbOaq$ (Mulder, *B.* 5, 1008).—4. *Hydroxylamine* forms acetoximic acid $CH_3.C(NOH).CH(NOH)$ (*v.* vol. i. p. 38).—5. *Water* at 200° gives lactic acid (Linnemann a. Zotta, *A.* 159, 218).—6. *Potash* splits it up into acetic and formic acids.—7. HCN gives the **cyanhydrin** $CH_3.C(OH)(CN).CHCl_2$ or the nitrile of di-chloro-oxy-isobutyric acid (Bischoff, *B.* 8, 1333).—8. Aqueous KCN gives crystalline tufts of $(C_3H_4Cl_2O)_2HCN$ (Glutz a. Fischer, *J. pr.* [2] 4, 52).

Isomeride of di-chloro-acetone $C_3H_4Cl_2O$. [44°]. (c. 168°). The entire product of the action of chlorine on cooled acetone has the composition of di-chloro-acetone, although it boils between 117° and 170°. This appears to be due to the presence of this crystalline isomeride. It only differs from *s*-di-chloro-acetone, derived from dichlorhydrin, in yielding with bromine a di-chloro-di-bromo-acetone identical with that obtained from *u*-di-chloro-acetone, and not with that obtained from the said *s*-di-chloro-acetone (Barbaglia, *B.* 7, 468; Cloez). This compound could not be obtained by Bischoff (*B.* 8, 1332).

Another isomeride $CHCl_2.\overset{O}{CH{:}CH_2}$ (?) *Chloro-epichlorhydrin* (?) (170°), is formed by chlorinating epichlorhydrin (Cloez, *A. Ch.* [6] 9, 115). With NH_3 it forms unstable $C_6H_9Cl_2NO_2$.

***s*-Di-chloro-acetone** $CH_2Cl.CO.CH_2Cl$. [41°]. (173° cor.). V.D. 63·2.

Formation.—1. By the oxidation of the corresponding dichlorhydrin of glycerin $CH_2Cl.CH(OH).CH_2Cl$ with $K_2Cr_2O_7$ and H_2SO_4. Purified by means of its crystalline compound with $NaHSO_3$ which is subsequently decomposed by Na_2CO_3. The yield is very small (Glutz a. Fischer, *J. pr.* [2] 4, 52; Hormann, *B.* 13, 1707; Markownikoff, *A.* 208, 349).—2. By the union of HClO with *α*-chloro-allyl chloride (di-chloro-propylene) $CH_2Cl.CCl{:}CH_2$ and HClO (Henry, *C. R.* 94, 1428).—3. From *s*-di-iodo-acetone and AgCl (Voelker, *A.* 192, 89).

Properties.—Long needles or trimetric tables. Extremely pungent; blisters the skin. M. sol. water, v. sol. alcohol and ether. With bisulphite of soda it forms long four-sided prisms of $C_3H_4Cl_2(OH)(SO_3Na)$ 3aq.

Reactions.—1. KI forms di-iodo-acetone [61°].—2. Dry KCN added to its ethereal solution forms crystalline tetra-chloro-di-acetone cyanhydrin $(C_6H_8Cl_4O_2)HCN$ which differs from the isomeric body obtained from *u*-di-chloro-acetone in being insol. water (G. a. F.).—3. HCN forms $(CH_2Cl)_2C(OH)CN$, the nitrile of di-chloro-oxy-isobutyric (di-chloro-acetonic) acid.—4. *Oxidised* by $K_2Cr_2O_7$ and H_2SO_4 to chloro-acetic acid.

According to Cloez (*A. Ch.* [6] 9, 145) successive treatment with bromine and $HgCl_2$ gives tetra-chloro-acetone, but the tetra-chloro-acetone prepared in this way from the di-chloro-acetone obtained from dichlorhydrin is different from that obtained from di-iodo-acetone. They also give different penta-chloro-acetones when treated with chlorine in sunlight. Cloez considers the derivative from dichlorhydrin to be a pseudo-di-chloro-acetone $CH_2Cl.\overset{O}{CH{:}CHCl}$. It does not combine with HOAc, but reacts violently with HCl, although the product, exposed over H_2SO_4, is re-converted into *ψ*-di-chloro-acetone.

Tri-chloro-acetone $CCl_3.CO.CH_3$. (180°) (Combes).

Formation.—Obtained in an impure state by passing chlorine into acetone that is not kept cool, especially if the chlorine be somewhat moist, or the acetone be mixed with methyl alcohol (crude wood spirit) (Bischoff, *B.* 8, 1331). The crude product of the oxidation of isobutyl alcohol with chromic mixture may also be used (Kramer, *B.* 7, 252).

Preparation.—1. By passing chlorine into an aqueous solution of sodium citraconate at 100° (Gottlieb a. Morawsky, *J. pr.* [2] 12, 369).—2. By the action of NaOH (1 mol.) upon hexa-*ω*-chloro-methylene di-methyl diketone (hexa-chloro-acetyl-acetone) $(CCl_3.CO)_2CH_2$ (Combes, *A. Ch.* [6] 12, 239).

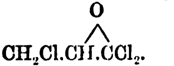
Properties.—Liquid, heavier than water, with fragrant odour. Converted by ammonia into chloroform and acetamide. Does not unite with $NaHSO_3$; but with HCN it forms $CCl_3.CMe(OH)CN$ (Bischoff). It unites readily with water, forming a hydrate $C_3H_3Cl_3O$ 2aq [44°] crystallising in four-sided prisms, which is resolved by distillation or by dry HCl into its constituents. The product of the chlorination of acetone boils at 172°, and has S.G. 1·418. According to Cloez it is a mixture; for it solidifies incompletely on cooling, when it deposits needles [c. −5°]. With aniline and KOH it gives phenyl-carbamine, showing the presence of $CCl_3.CO.CH_3$. Successive treatment with ammonia and KOH gives di-chloro-methyl-amine, indicating the presence of $CHCl_2.CO.CH_2Cl$.

Tri-chloro-acetone $CHCl_2.CO.CH_2Cl$. (172°). From *u*-di-chloro-acetone by treating with bromine and heating the resulting $CHCl_2.CO.CH_2Br$ with $HgCl_2$ in presence of alcohol (Cloez). Gives no chloroform with ammonia, nor phenyl-carbamine with aniline and KOH.

***u*-Tetra-chloro-acetone** $CH_2Cl.CO.CCl_3$. (181°). S.G. ^{17} 1·482. Formed by saturating acetone containing methyl alcohol or wood spirit with chlorine in daylight, the temperature being allowed to rise (Bonis, *A. Ch.* [3] 21, 111). The fraction boiling at 160°–180° is exposed to a low temperature in contact with water, whereupon the hydrate of tri-chloro-acetone crystallises out first, then a compound of this with tetra-chloro-acetone hydrate $(C_3H_3Cl_3O)(C_3H_2Cl_4O)$ 6aq [32°], and finally large prisms of the hydrate of tetra-chloro-acetone $C_3H_2Cl_4O$ 4aq [39°] (c. 179°), which may be resolved by dry HCl into tetra-chloro-acetone and water.

Properties.—Colourless hygroscopic liquid, sol. water, with pungent odour. Readily volatile with steam. Turned brown by air and light. Partially decomposed by distillation. With aniline and KOH it yields phenyl carbamine. Aqueous ammonia at a low temperature forms chloroform and chloro-acetamide.

***s*-Tetra-chloro-acetone** $CHCl_2.CO.CHCl_2$. (180°). S.G. ^{14} 1·48. Formed by treating *u*-di-chloro-acetone, or the *s*-di-chloro-acetone derived from *s*-di-iodo-acetone, with bromine and decomposing the resulting $CHCl_2.CO.CHBr_2$ with $HgCl_2$ in alcoholic solution at 100°. Purified by conversion into its crystalline hydrate [48°] and subsequent dehydration by dry HCl (Cloez). This tetra-chloro-acetone does not give the chloroform and carbamine reactions. The di-chloro-di-bromo-derivative obtained by the action of bromine on dichlorhydrin yields with $HgCl_2$ an oil which is not attacked by ammonia. The product of the oxidation of dichlorhydrin gives with bromine $CHClBr.CO.CHClBr$ (Markownikoff), whence $HgCl_2$ gives a fuming liquid (180°); this liquid does not combine with $NaHSO_3$, but yields with ammonia di-chloro-acetamide, and with aniline di-chloro-acetanilide. Cloez considers that it is isomeric, but not identical with *s*-tetra-chloro-acetone ; thus it might be



$CH_2Cl.\overset{\overset{O}{\wedge}}{CH.CCl_2}$.

Penta-chloro-acetone $CCl_3.CO.CHCl_2$. (192°). S.G. $\frac{14}{4}$ 1·576. S. 15.

Formation.— 1. By passing chlorine into a strong solution of sodium citraconate (Plantamour, *Gm.* 11, 440).- 2. By the action of HCl and $KClO_3$ on various organic compounds, *e.g.* quinic, citric, gallic, and salicylic acids, pyrogallol, quinone, indigo, tyrosine, and muscular flesh (Städeler, *A.* 111, 277).—3. By the action of chlorine in sunlight upon commercial acetone or on di-chloro acetone (Cloez, sen., *A.* 111, 180; Cloez, jun., *Bl.* [2] 39, 637). Pure acetone gives only di-chloro-acetone when chlorinated at 100° in sunlight (Fittig).

Preparation.—A solution of citric acid in $1\frac{1}{2}$ pts. water is allowed to fall drop by drop down a tube packed with pumice heated to 100°, up which a current of dry chlorine is passing (Cloez, jun , *A. Ch.* [6] 9, 145).

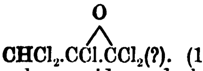
Properties.— Colourless liquid, smelling (after exposure to air) like chloral. With water at 4° it forms a crystalline hydrate C_3HCl_5O 4aq [15°], which, on fusion, separates into water and penta-chloro-acetone. Penta-chloro-acetone separates completely from its aqueous solution at 60°. Penta-chloro-acetone dissolves a little water, but on warming this separates as globules.

Reactions.—1. *Ammonia* gives chloroform and di-chloro-acetamide [95°] (235°).—2. *Aniline* and KOH give phenyl-carbamine.—3. KOH gives di-chloro-acetic acid, KCl, and K_2CO_3.

Isomeride of penta-chloro-acetone

$\overset{\overset{O}{\wedge}}{CCl_3.CH.CCl_2}$(?). *Tetra-chloro-epichlorhydrin.* (185°). S.G. $\frac{8}{4}$ 1·617. By the action of chlorine in sunlight on the *s*-di-chloro-acetone from di-chlorhydrin (Cloez, jun., *Bl.* [2] 39, 639). Pungent liquid. With ammonia it gives tri-chloro-acetamide [139°] (235°–240°) but no chloroform.

Another isomeride of penta-chloro-acetone



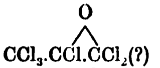
$CHCl_2.\overset{\overset{O}{\wedge}}{CCl.CCl_2}$(?). (178°). From di-chloro-propylene oxide and chlorine (Cloez, jun., *A. Ch.* [6] 9, 145). Fuming liquid. With ammonia it gives di-chloro-acetamide, but no chloroform.

Hexa-chloro-acetone $CCl_3.CO.CCl_3$. [–2°]. (203°). S.G. ^{12} 1·744. V.D. 9·62. Formed by saturating a conc. aqueous solution of citric acid with chlorine in sunshine (Plantamour, *B. J.* 26, 428). The yield is 25 p.c. of the weight of citric acid. Formed also by the action of chlorine on (commercial) acetone in sunlight. On distilling the product a considerable quantity of hexa-chloro-benzene is usually formed.

Properties.—Limpid liquid, which has a feeble odour in the cold, but becomes very pungent when warmed. Solidifies when cooled in large plates. Sl. sol. water. Forms a crystalline hydrate C_3Cl_6O aq [15°] almost insol. water.

Reactions.– 1. With aqueous *ammonia* it forms chloroform and tri-chloro-acetamide.—2. *Aniline* forms chloroform and tri-chloro-acetanilide.—3. *Water* at 120° splits it up into chloroform and tri-chloro-acetic acid. –4. *Potash* gives CO_2 and tri-chloro-acetic acid.—5. With *o-toluidine* it forms tri-chloro-acetyl *o*-toluidine $C_6H_4Me.NH.CO.CCl_3$ [67°]; with *p-toluidine* it forms the isomeric body [80°].—6. *Diethylamine* gives $NEt_2.CO.CCl_3$ [90°].—7. *Allylamine* forms $NHC_3H_5.CO.CCl_3$ [45°].—8. *Ethylene-diamine* gives $NH_2.C_2H_4.CO.CCl_3$ [200°].—9. *Urea* (1 mol.) at 150° forms $CO(NH.CO.CCl_3)_2$.

Isomeride of hexa-chloro-acetone

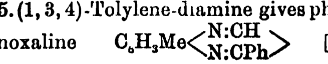


$CCl_3.\overset{\overset{O}{\wedge}}{CCl.CCl_2}$(?) (c. 205°). This substance appears to be formed, together with hexa-chloro-benzene, by the action of chlorine on epichlorhydrin in sunlight (Cloez, jun.).

CHLORO-ACETONIC ACID *v.* CHLORO-OXY-ISOBUTYRIC ACID.

CHLORO-ACETONITRILE *v.* *Nitrile of* CHLORO-ACETIC ACID.

ω-CHLORO-ACETOPHENONE $C_6H_5.CO.CH_2Cl$. *Phenacyl chloride. Phenyl chloro-methyl ketone.* [59°]. (215°). Formed, together with di- and tri-chloro-acetophenone, by passing chlorine into boiling acetophenone. The fraction (240°–250°) solidifies on cooling, and is recrystallised from dilute alcohol (Gräbe, *B.* 4, 35; Städel, *B.* 10, 1830; Gautier, *C. R.* 102, 1248). Colourless trimetric plates; *a*:*b*:*c* = ·9957:1:·2135 (Friedländer); v. e. sol. alcohol and ether, insol. water. Its vapour is pungent.

Reactions.—1. KOAc forms the acetyl derivative of ω-oxy-acetophenone, $C_6H_5.CO.CH_2OAc$. 2. PCl_5 forms di-chloro-styrene $C_6H_5.CCl:CHCl$.—3. *Chromic acid* oxidises it to benzoic acid.—4. *Ammonia* passed into its ethereal solution forms two isomerides $C_{10}H_{11}ClO_2$ [117°] and [155°]. Boiling aqueous ammonia forms (α)-phenyl-amphinitrile or isoindole $C_{16}H_{14}N_2$ [195°], which crystallises from alcohol in blue monoclinic needles (V. Meyer a. Treadwell, *B.* 16, 342).—5. (1, 3, 4)-Tolylene-diamine gives phenyl-toluquinoxaline  $C_6H_3Me\left\langle\begin{matrix}N:CH\\N:CPh\end{matrix}\right\rangle$ [135°] (Hinsberg, *A.* 237, 370).

p-**Chloro-acetophenone** [4:1]$C_6H_4Cl.CO.CH_3$. *Chloro-phenyl methyl ketone.* [20°]. (231°). S.G. ^{20} 1·19. From chloro-benzene, acetyl chloride, and Al_2Cl_6 (Gautier, *Bl.* [2] 43, 602). V. sl. sol. water, miscible with alcohol and ether. $KMnO_4$ oxidises it to *p*-chloro-benzoic acid.

Di-ω-chloro-acetophenone $C_6H_5.CO.CHCl_2$. (248°). S.G. ^{15} 1·338. From di-chloro-acetyl chloride, benzene, and Al_2Cl_6 (Gautier, *C. R.* 103, 812).

Tri-ω-chloro-acetophenone $C_6H_5.CO.CCl_3$. (249°). S.G. ^{16} 1·427. From tri-chloro-acetyl chloride (60 g.), benzene (100 g.), and Al_2Cl_6 (Gautier, *C. R.* 103, 812). Oil; slowly oxidised by $KMnO_4$ to benzoic acid.

TRI-ω-CHLORO-ACETOPHENONE *o*-CARBOXYLIC ACID $CCl_3.CO.C_6H_4.CO_2H$. [144°]. Formed by passing chlorine into a hot solution of phthalyl-acetic acid in diluted HOAc (Michael a. Gabriel, *B.* 10, 1556). Decomposed by alkalis into chloroform and phthalic acid.

CHLORO-ACETOTHIENONE *v.* THIENYL CHLORO-METHYL KETONE.

CHLORO-ACETOXIM $(CH_3)_2C:NOCl$. *Acetchloroxim.* (134° uncor.); when quickly heated it explodes with violence. V.D. 4·1 (for 3·7). Obtained by adding a solution of hypochlorous acid to an aqueous solution of acetoxim at 0°; the liquid that separates is washed with water, and dried over $CaCl_2$. Colourless mobile liquid of pleasant odour, which solidifies in a freezing-mixture of solid CO_2 and ether, to colourless prisms. V. sol. alcohol and ether, v. sl. sol. water. Warmed with HCl or HI it sets free the halogens (Mohlau a. Hoffmann, *B.* 20, 1505).

TRI-CHLORO-β-ACETYL-ACRYLIC ACID *v.* TRI-CHLORO-PHENOMALIC ACID.

TRI-CHLORO-ACETYL-BENZOIC ACID *v.* TRI-CHLORO-ACETOPHENONE CARBOXYLIC ACID.

CHLORO-ACETYL BROMIDE $CH_2Cl.CO.Br$. (127°) (W.); (134°) (G.). S.G. $\frac{0}{0}$ 1·913. Prepared by adding bromine (160 g.) to chloro-acetic acid (94 g.) and red phosphorus (15 g.) (De Wilde, *A.* 130, 372; 132, 173; Gal, *A.* 132, 180). Fuming liquid. With water it forms HBr and chloro-acetic acid; alcohol gives EtBr and chloro-acetic ether.

Tri-chloro-acetyl bromide $CCl_3.CO.Br$. (140°) (H.); (143°) (G.). S.G. $\frac{15}{15}$ 1·900. From PBr_3 (2 mol.) and tri-chloro-acetic acid (3 mol.). 300 grms. of the acid give 200 grms. bromide (Hofferichter, *J. pr.* 128, 196; Gal, *C. R.* 76, 1019; *Bl.* [2] 20, 11). Water decomposes it into HBr and tri-chloro-acetic acid; alcohol gives EtBr and tri-chloro-acetic ether.

CHLORO-ACETYL CHLORIDE $CH_2Cl.CO.Cl$. Mol. w. 113. (107°). S.G. $\frac{0}{0}$ 1·495. Formed by the action of chlorine on acetyl chloride in sunlight (Wurtz, *A.* 102, 93); or, together with di-chloro-acetyl chloride by boiling acetyl chloride with PCl_5 (Michael, *J. pr.* [2] 35, 95). Formed also by treating chloro-acetic acid with PCl_3 (De Wilde, *A.* 130, 372). Liquid, converted by water into HCl and chloro-acetic acid; and by dry ammonia into chloro-acetamide.

Reactions.—1. Successive treatment with *zinc methyl* and water forms methyl-isopropyl-carbinol (Bogomoletz, *Bl.* [2] 34, 330).—2. With *o-amido-phenol* it forms $C_6H_4(OH).NH.CO.CH_2Cl$ [136°] (Aschan, *B.* 20, 1523). It reacts similarly with other amido-compounds.—3. *Phosphuretted hydrogen* forms chloro-acetyl-phosphide $CH_2Cl.CO.PH_2$, a white powder slowly decomposed by water into PH_3 and chloro-acetic acid (Steiner, *B.* 8, 1178).

Di-chloro-acetyl chloride $CHCl_2.CO.Cl$. Mol. w. 147½. (108°). Formed by the action of PCl_5 on di-chloro-acetic acid (Otto a. Beckurts, *B.* 14, 1618); or, together with the preceding, by boiling acetyl chloride with PCl_5 (M.). Pungent, fuming liquid: decomposed at once by water. Successive treatment with $ZnMe_2$ and water forms (6 p.c. of) di-methyl-propyl-carbinol (B.).

Tri-chloro-acetyl chloride $CCl_3.CO.Cl$. (117·9°) (Thorpe, *C. J.* 37, 189). S.G. $\frac{0}{4}$ 1·6564. C.E. (0°–10°) ·001095; (0°–100°) ·0012013. S.V. 125·51.

Formation.—1. From PCl_3 and $CCl_3.CO_2H$ (Gal, *C. R.* 76, 1019). The yield is very small. 2. By the protracted action of chlorine on ether, the operation being conducted towards the end in sunlight (Malaguti, *A. Ch.* [3] 16, 5). Also by the distillation of penta-chloro-ethyl ether $(C_2Cl_5)_2O$, or of perchlorinated acetic ether $CCl_3.CO_2C_2Cl_5$.—3. Together with SO_2 from C_2Cl_4 and SO_3 at 150° (Prudhomme, *C. R.* 70, 1137). Also from C_2Cl_6 and SO_3.

Properties.—Liquid; decomposed by water into HCl and tri-chloro-acetic acid; alcohol gives tri-chloro-acetic ether.

Reactions.—1. *Zinc methide* followed by water gives the heptyl alcohol $CMe_3.CMe_2OH$ (B.).—2. PH_3 gives $CCl_3.CO.PH_2$ (Steiner, *B.* 8, 1178; Cloez, *A. Ch.* [3] 17, 309).—3. *Tri-chloro-acetic acid* forms the anhydride $(CCl_3.CO)_2O$ (Anschütz, *B.* 10, 1881).

TRI-CHLORO-ACETYL CYANIDE $CCl_3.CO.CN$. *Tri-chloro-pyruvonitrile.* (118°) (H.); (122°) (C. a. A.). S.G. $\frac{15}{}$ 1·559.

Preparation.—1. By adding AgCy slowly to cooled tri-chloro-acetyl bromide; the reaction being finished by heating on a water-bath (Hofferichter, *J. pr.* 128, 200).—2. By boiling tri-chloro-acetyl bromide with mercurous cyanide (Claisen a. Antweiler, *B.* 13, 1935).

Properties.—Pungent, hygroscopic liquid smelling of prussic acid. Exposed to air it first becomes crystalline (forming a hydrate?) then deliquesces.

Reactions.—1. *Water* decomposes it into tri-chloro-acetic acid and prussic acid.—2. HCl (S.G. 1·16) at 50° converts it into tri-chloro-pyruvic acid $CCl_3.CO.CO_2H$.

Polymeride $(CCl_3.CO.CN)_x$. [140°]. From AgCy and tri-chloro-acetyl bromide at 150° (H.). Dimetric tables (from ether-alcohol); insol. water.

CHLORO-ACETYLENE $CH\vdots CCl$. Formed by boiling β-di-chloro-acrylic acid $CCl_2:CH.CO_2H$ with baryta-water (Wallach, *A.* 203, 87). Gas, which explodes spontaneously, forming carbon and HCl. It is stable when diluted with hydrogen, and then, when passed into bromine, forms crystalline C_2HClBr_4. With ammoniacal cuprous chloride it forms an orange pp., and in ammoniacal silver nitrate a white pp. These pps. explode violently when heated.

TRI-CHLORO-ACETYL IODIDE $CCl_3.CO.I$. (c. 180°). From tri-chloro-acetic acid and PI_3 (Gal, *C. R.* 76, 1019).

CHLORO-ACETYL-PROPIONIC ACID $C_5H_7ClO_3$. *Chloro-levulic acid.*

Ethyl ether A′Et (225°–230°), S.G. $\frac{21}{15}$ 1·196. Prepared from β-acetyl-propionic ether $CH_3.CO.CH_2.CH_2.CO_2Et$ and chlorine. Colourless pungent liquid (Conrad a. Guthzeit, *B.* 17, 2286).

CHLORO-ACETYL-UREA $NH_2.CO.NH.CO.CH_2Cl$. From urea and chloro-acetyl chloride (Tommasi, *C. R.* 76, 640). Thin needles (from alcohol). Sl. sol. boiling water. With thio-urea it forms urea, HCl, and thio-hydantoin.

Tri-chloro-acetyl-urea $NH_2.CO.NH.CO.CCl_3$. [150°]. Formed by heating tri-chloro-acetyl chloride with urea (Tommasi a. Meldola, *C. J.* 27, 404), or urea tri-chloro-acetate with P_2O_5 (De Clermont, *C. R.* 78, 848). Needles or plates; insol. cold water.

CHLORO- ACIDS *v.* CHLORO- COMPOUNDS.

α-CHLORO-ACRYLIC ACID $C_3H_3ClO_2$ *i.e.* $CH_2:CCl.CO_2H$. [65°]. (c. 178°).

Formation.—1. From αβ-di-chloro-propionic acid $CH_2Cl.CHCl.CO_2H$ by treatment with baryta or alcoholic KOH (Werigo, *A.* 170, 168; *B.* 10, 1499).—2. From α-di-chloro-propionic acid $CH_3.CCl_2.CO_2H$ and alcoholic KOH (Otto a. Beckurts, *B.* 18, 239).

Properties.—Needles; v. sol. water, but may be extracted by ether. Fuming HCl at 100° forms αβ-di-chloro-propionic acid.

Salts.—AgA': white crystalline pp.—KA'aq: needles.—BaA'$_2$2aq: plates.

β-Chloro-acrylic acid CHCl·CH.CO$_2$H. [84°].

Formation.—1. From ethyl tri-chloro-lactate (or from chloralide), zinc, and HCl in alcoholic solution (Pinner a. Bischoff, *A.* 179, 85; Wallach a. Hunaeus, *A.* 193, 23).—2. By combination of propiolic acid with HCl (Bandrowsky, *B.* 15, 2702).

Preparation.—From chloralide (50 g.), alcohol (150 g.), Zn (80 g.), HCl (80 g. of S.G. 1·21). The reaction is moderated by cooling, and after 24 hours more HCl (20 g.) and Zn (15 g.) are added. After 24 hours HCl (30 g.) is added. The alcohol and by-products are evaporated off and the remaining solution is extracted with benzene. The β-chloro-acrylic acid which is dissolved is subsequently distilled with steam. 1,000 g. of chloralide yield 12 g. of β-chloro-acrylic acid (Otto a. Fromme, *A.* 239, 264).

Properties.—Flexible laminæ, m. sol. chloroform, v. sol. water, v. e. sol. benzene. Above 15° it separates from aqueous solution in oily drops. Aqueous HCl at 80° gives CHCl$_2$.CH$_2$.CO$_2$H. Combines with bromine (1 mol.).

Salt.—AgA'.

Ethyl ether EtA'. (144°).

αβ-Di-chloro-acrylic acid CHCl:CCl.CO$_2$H. [86°].

Formation.—1. By the action of KOH on mucochloric acid (Hill, *Am.* 3, 168; *B.* 12, 656). **2.** By heating per-chloro-pyrocoll octo-chloride or di-chloro-maleimide with water at 130° (Ciamician a. Silber, *B.* 16, 2392).

Properties.—Monoclinic prisms; *a:b:c* = 1·1865:1:·3637 (Hill a. Melville, *P. Am. A.* 17, 131). Volatilises rapidly in the air. V. e. sol. water, alcohol, and ether; v. sl. sol. benzene.

Salts.—AgA': slender needles.—KA': felted needles.—BaA'$_2$aq: trimetric plates. S. 6·6 at 18°.—CaA'$_2$ 3aq: soluble needles.

β-Di-chloro-acrylic acid CCl$_2$:CH.CO$_2$H(?) [77°] and [64°]. This acid may possibly be *allo*-αβ-di-chloro-acrylic acid. Formed, together with β-chloro-acrylic acid, by reducing chloralide in alcoholic solution with Zn and HCl (Wallach, *A.* 193, 20; 203, 84). Slender needles or monoclinic prisms (from chloroform). Volatile in air; but cannot be distilled. After heating to 120° it melts at 64°, but, on keeping, the melting-point rises to 77°. V. sl. sol. water; v. sol. ether and chloroform. Does not combine directly with Br. Not attacked by water at 200°. Boiling baryta-water forms chloro-acetylene.

Salts. KA'.—AgA'.—CaA'$_2$2aq. ZnA'$_2$2aq.

Ethyl ether EtA'. (174°). Saponified by cold KOHAq. Converted by treatment with Ag$_2$O at 125° and saponification of the product by Ca(OH)$_2$ into malonic acid.

Chloride CCl$_2$:CH.COCl. (Above 145°).

Amide CCl$_2$:CH.CONH$_2$. [113°]. Needles.

Tri-chloro-acrylic acid CCl$_2$:CCl.CO$_2$H. [76°]. S. 6 at 20°. From tri-chloro-bromo-propionic acid and cold baryta-water (Mabery, *Am.* 9, 3). Trimetric prisms, sl. sol. water, m. sol. hot CS$_2$, v. sol. alcohol, ether, and chloroform.

Salts.—KA': irregular plates, sl. sol. cold water.—AgA': slender needles, v. sl. sol. cold water.—CaA'$_2$3½aq: tufts of needles.—BaA'$_2$ 3½aq: branches of pearly needles.

CHLORO-ALDEHYDE *v.* CHLORO-ACETIC ALDEHYDE.

CHLORO-ALDOXIM CH$_3$.CH:NOCl. Formed by mixing solutions of aldoxim and hypochlorous acid; the liquid which separates being washed with water and dried over CaCl$_2$. Colourless liquid of powerful odour. Very unstable. Decomposes explosively on heating. Liberates iodine from HI (Mohlau a. Hoffmann, *B.* 20, 1507).

CHLORO-ALIZARIN *v.* CHLORO-DI-OXY-ANTHRAQUINONE.

CHLORO-DIALLYL *v.* HEXINYL CHLORIDE.

α-CHLORO-ALLYL ACETATE CH$_2$:CCl.CH$_2$.OAc. (145°). Formed in small quantity, with other products, by the action of KOAc on di-chloro-propylene CH$_2$:CCl.CH$_2$Cl (Henry, *B.* 5, 154).

β-Chloro-allyl acetate CHCl:CH.CH$_2$OAc. (c. 158°). From di-chloro-propylene CHCl:CH.CH$_2$Cl and KOAc (Martinoff, *B.* 8, 1318).

α-CHLORO-ALLYL ALCOHOL C$_3$H$_5$ClO *i.e.* CH$_2$:CCl.CH$_2$OH. (136°) (H.); (c. 138° i. V.) (R.). S.G. ^{12} 1·164. Formed by boiling di-chloro-propylene CH$_2$:CCl.CH$_2$Cl (95°) with a dilute solution of K$_2$CO$_3$ for some hours (Henry, *C. R.* 95, 849). Formed also by the action of dilute KOH or Ag$_2$O upon α-chloro-allyl iodide CH$_2$:CCl.CH$_2$I (Van Romburgh, *R. T. C.* 1, 233).

Liquid with faint aromatic odour. Does not attack the skin. M. sol. water; gives α-chloro-allyl acetate (145°) with Ac$_2$O. When distilled with much water α-chloro-allyl alcohol yields acetyl-carbinol CH$_3$.CO.CH$_2$OH. HClO gives CH$_2$Cl.CO.CH$_2$OH.

β-chloro-allyl alcohol CHCl:CH.CH$_2$OH. (153° cor.). S.G. ^{15} 1·162. V.D. 3·3. Formed by treating CHCl.CH.CH$_2$Cl with aqueous KOH at 100° (Romburgh, *Bl.* [2] 36, 555). Pungent liquid, sl. sol. water. Blisters the skin. Combines with bromine.

DI-CHLORO-DI-ALLYL-AMINE C$_6$H$_9$Cl$_2$N *i.e.* (CH$_2$:CCl.CH$_2$)$_2$NH(?) (194°). From *s*-tri-chloro-propane and alcoholic ammonia by heating for a few days at 110° (Engler, *Bl.* [2] 9, 134; *A.* 142, 72). Heavy oil, sl. sol. water.—B'HCl: deliquescent needles. B'$_2$H$_2$PtCl$_6$.

Tetra-chloro-di-allyl-amine C$_6$H$_7$Cl$_4$N *i.e.* (CHCl:CCl.CH$_2$)$_2$NH. From CH$_2$Cl.CCl$_2$.CH$_2$Cl and alcoholic NH$_3$ at 120° (Fittig a. Pfeffer, *A.* 135, 363). Alkaline liquid; cannot be distilled; volatile with steam; sl. sol. water.—B'HCl: needles. B'H$_2$C$_2$O$_4$.

CHLORO-ALLYL-BROMIDE *v.* CHLORO-BROMO-PROPANE.

CHLORO-ALLYL-CHLORIDE *v.* DI-CHLORO-PROPANE.

CHLORO-ALLYLENE *v.* PROPARGYL CHLORIDE.

CHLORO-ALLYL ETHYL OXIDE *v.* ETHYL CHLORO-ALLYL OXIDE.

CHLORO-ALLYL IODIDE *v.* CHLORO-IODO-PROPANE.

α-CHLORO-ALLYL NITRATE C$_3$H$_4$ClNO$_3$ *i.e.* CH$_2$:CCl.CH$_2$.NO$_3$. (140°). From α-chloro-allyl alcohol, H$_2$SO$_4$, and HNO$_3$ (Henry, *C. R.* 95, 849), or from α-chloro-ω-iodo-propane CH$_2$:CCl.CH$_2$I and AgNO$_3$. Oil (Romburgh, *R. T. C.* 1, 238).

α-CHLORO-ALLYL THIOCARBIMIDE C$_4$H$_4$ClNS *i.e.* CH$_2$:CCl.CH$_2$.NCS. (181°). From CH$_2$:CCl.CH$_2$Cl and potassium sulphocyanide

(Henry, *C. R.* 95, 849; *Bl.* [2] 39, 526). Liquid, smelling like mustard. Converted by ammonia into chloro-allyl thio-urea [91°].

CHLORO-ALLYL THIO-UREA $C_4H_7ClN_2S$ *i.e.* $CH_2:CCl.CH_2.NH.CS.NH_2$. [91°]. Prepared as above (Henry, *B.* 5, 188).

CHLORO-AMIDES *v.* CHLORO-COMPOUNDS.

DI-CHLORO-AMIDO-ACETIC ETHER $C_4H_7Cl_2NO_2$ *i.e.* $CCl_2(NH_2).CO_2Et$. *Di-chloro-glycocoll. Oxamethane chloride.* From oxamic ether and PCl_5 (Wallach, *A.* 184, 8). Unstable crystals, splitting off HCl and leaving $NH:CCl.CO_2Et$, and finally $N\vdots C.CO_2Et$.

Reactions.—1. *Water* forms HCl and oxamic ether. -2. *Butyl alcohol* forms butyl oxamate; other alcohols and phenols act similarly.—3. $POCl_3$ forms $NH(POCl_2).CCl_2.CO_2Et$ [130°], which may be crystallised from chloroform or ligroin, but is decomposed by water or heat.

m-**CHLORO-AMIDO-BENZENE** (*a*)-**SULPHONIC ACID** $C_6H_6ClNSO_3$ *i.e.* $C_6H_3(Cl)(NH_2)(SO_3H)$ [1 3:?]. Prepared by reducing *m*-chloro-nitro-benzene (*a*)-sulphonic acid with ferrous hydrate. Colourless soluble needles (Post a. Meyer, *B.* 14, 1607).

m-**Chloro-amido-benzene** (*β*)-**sulphonic acid** $C_6H_3(Cl)(NH_2)(SO_3H)$ [1:3:?]. Prepared by reduction of *m*-chloro-nitro-benzene (*β*)-sulphonic acid with ferrous hydrate. Plates, sl. sol. water.

Salts.—$NaA'2aq$: colourless needles.—$BaA'_2 7\frac{1}{2}aq$: colourless thick needles, v. sol. water and alcohol (Post a. Meyer, *B.* 14, 1607).

m-**Chloro-amido-benzene** (*γ*)-**sulphonic acid** $C_6H_3(Cl)(NH_2)(SO_3H)$ [1:3:?]. Prepared by sulphonation of *m*-chlor-aniline. Sparingly soluble crystals.

Salts.—$NaA'\frac{1}{2}aq$: yellowish needles.—$NaA'2aq$: colourless needles.—BaA'_2aq: small yellow needles, sol. alcohol.—$SrA'_2 9aq$: long colourless needles, sol. alcohol and water (Post a. Meyer, *B.* 14, 1607).

Di-chloro-amido-benzene sulphonic acid $C_6H_2Cl_2(NH_2)(SO_3H)$. From amido-benzene *m*-sulphonic acid and chlorine (Beckurts, *A.* 181, 212). Slender needles (containing 2aq): sl. sol. water.

CHLORO-*o*-AMIDO-BENZOIC ACID $C_6H_3Cl(NH_2)(CO_2H)$ [1:4:5]. *Chloro-anthranilic acid.* [204°].

Formation.—From chloro-isatoic acid and conc. HCl (Drosch, *J. pr.* [2] 33, 50).

Properties.—Long white needles (from alcohol). V. sol. glacial acetic acid, acetone, and alcohol, sol. ether, benzene, and water containing HCl, m. sol. chloroform, sl. sol. water. Its solutions have a yellowish colour and exhibit violet fluorescence.

Amide $C_6H_3Cl.(NH_2).CO.NH_2$. [172°]. By the action of hot NH_3Aq upon chloro-isatoic acid. Flat needles (from alcohol or from water). Sol. alcohol, acetone, and glacial acetic acid, less sol. chloroform, ether, benzene, and water.

Chloro-*o*-amido-benzoic acid $C_6H_3Cl(NH_2)(CO_2H)$ [1:2:3]. *Chloro-anthranilic acid.* [148°]. From chloro-nitro-benzoic acid [136°] by reduction (Cunze a. Hubner, *A.* 135 111; Hübner a. Weiss, *B.* 6, 175). Long needles, v. sl. sol. water.—$KA'2aq$.—AgA'.—$CaA'_2 1\frac{1}{2}aq$.—$BaA'_2 1\frac{1}{2}aq$.—PbA'_2.

Chloro-*m*-amido-benzoic acid $C_6H_3Cl(NH_2)CO_2H$ [1:2:4]. [212°]. Obtained by reducing the nitro-acid [180°] (Reveill, *A.* 222, 184). Formed also by boiling the diazo-imide of benzoic acid with HCl (Griess, *B.* 19, 315). Reduced by sodium amalgam to *m*-amido-benzoic acid. Salts.—PbA'_2.—CuA'_2.—$HA'H_2SO_4$.

Chloro-*m*-amido-benzoic acid $C_6H_3Cl(NH_2)CO_2H$ [1:2:6]. [185°]. Formed together with the [1:3:4] isomeride by boiling the *m*-diazo-imide of benzoic-acid $C_6H_4N_3.CO_2H$ with HCl (Griess, *B.* 19, 315). White tables or small prisms. V. sol. hot water.

Chloro-*m*-amido-benzoic acid $C_6H_3Cl(NH_2)CO_2H$ [1:4:6]. [212°]. From the nitro-acid [165°] by Sn and HCl (Wilkens a. Rack, *A.* 222, 198). Brownish needles (from water); v. sol. water or alcohol. Reduced by sodium amalgam to *m*-amido-benzoic acid.

Salts.—$PbA'_2 1\frac{1}{2}aq$.—$(A'Cu)_2O$.—$HA'HCl$.—$HA'H_2SO_4$.—$HA'HNO_3$.

s-**Chloro-*m*-amido-benzoic acid** $C_6H_3Cl(NH_2)CO_2H$ [1:3:5]. [216°]. From $C_6H_3Cl(NO_2)CO_2H$ [147°], Sn, and HCl (Hubner, *A.* 222, 90). Long needles; v. sol. alcohol or ether, sl. sol. water.

Salts.—$BaA'_2 4aq$.—AgA'.—CuA'_2.

Di-chloro-*o*-amido-benzoic acid $C_6H_2Cl_2(NH_2)CO_2H$ [1:2:4:5]. *Di-chloro-anthranilic acid.* [222°-224°]. Formed by boiling di-chloro-isatoic acid with conc. HCl (Dorsch, *J. pr.* [2] 33, 52). Needles. V. sol. ordinary solvents, except water.

Amide $C_6H_2Cl_2(NH_2)CO.NH_2$. [284°]. From di-chloro-isatoïc acid and aqueous ammonia. Short thick needles (from alcohol-acetone). Sl. sol. all solvents.

Tri-chloro-amido-benzoic acid $C_6HCl_3(NH_2)(CO_2H)$ [1:3:5:2:4]. [210°]. From tri-chloro-nitro-benzoic acid, tin, and HCl (Beilstein a. Kuhlberg, *A.* 152, 240) Small slender needles (from water); sl. sol. boiling water. Does not unite with acids.—$BaA'_2 3aq$.

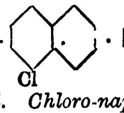
Tetra-chloro-amido-benzoic acid $C_6Cl_4(NH_2).CO_2H$ [1:2:3:4:5:6]. *Tetra-chloro-anthranilic acid.* Obtained by reduction of tetra-chloro-nitro-benzoic acid with tin and HCl. Colourless amorphous solid. V. sol. alcohol, nearly insol. water (Tust, *B.* 20, 2441).

DI-CHLORO-*o*-AMIDO-BENZOIC ALDEHYDE $C_6H_2Cl_2(NH_2)CHO$. [78°]. Obtained by reduction of di-chloro-nitro-benzaldehyde with $FeSO_4$ and NH_3 (Gnehm, *B.* 17, 754). Yellow needles. Sl. sol. water.

CHLORO-AMIDO-NAPHTHALENE *v.* CHLORO-NAPHTHYLAMINE.

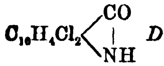
Chloro-di-amido-naphthalene *v.* CHLORO-NAPHTHYLENE-DIAMINE.

CHLORO-AMIDO-(*a*)-NAPHTHOIC LACTAM $C_{11}H_6ClNO$ *i.e.*



. [270°]. *Chloro-amido-(a)-naphthoid. Chloro-naphthostyril.* Formed by reduction of chloro-nitro-(*a*)-naphthoic acid [225°] with $FeSO_4$ and NH_3. Yellow needles (from alcohol) (Ekstrand, *B.* 18, 2831).

Di-chloro-amido-naphthoic lactam



$C_{10}H_4Cl_2\left<\begin{matrix}CO\\ |\\ NH\end{matrix}\right.$ *Di-chloro-naphthostyril.* [265°].

Formed by chlorination of the lactam of amido-(α)-naphthoic acid. Also by heating nitro-(α)-naphthoic acid [215°] with excess of fuming HCl for two hours at 140°-150°. Yellow needles (from acetic acid). Sl. sol. alcohol (Ekstrand, *B.* 19, 1132).

CHLORO-*o*-AMIDO-PHENOL

$C_6H_3Cl(NH_2)(OH)$ [1:3.4]. From chloro-*o*-nitro-phenol, tin, and HCl (Faust a. Saame, *A. Suppl.* 7, 193).—B'HCl: laminæ (from water).

Methyl ether $C_6H_3Cl(NH_2)(OMe)$. *Chloro-anisidine* [52°]. (260°). From the nitro- compound. White needles or prisms. Sol. alcohol, ether, and benzene. Salts.—B'HCl: colourless soluble needles.—$B_2H_2Cl_2PtCl_4$: soluble yellow needles.

Picrate $B'C_6H_2(NO_2)_3OH$: [about 200°]; yellow needles, sol. alcohol and ether, sl. sol. water.

Acetyl derivative [150°], (326°), glistening plates (Herold, *B.* 15, 1685).

Chloro-*p*-amido-phenol $C_6H_3Cl(NH_2)(OH)$ [1:3:6]. [153°]. From *p*-nitro-phenol by treatment with $KClO_3$ and HCl and reducing the product with tin and HCl (Kollrepp, *A.* 234, 6). Unstable needles, v. sol. alcohol and ether. Bleaching powder and HCl give chloro-quinone chlorimide $C_6H_3Cl(NCl)O$. Salts.—B'HCl: trimetric plates. — $B'_2H_2SO_4$ 2aq: scales.—$B'H_2C_2O_4$ 3½ aq: needles.—Tartrate $B'C_4H_6O_6$: monoclinic crystals, insol. water.

Di-chloro-*o*-amido-phenol

$C_6H_2Cl_2(NH_2)(OH)$ [1:3:5:6]. From di-chloro-nitro-phenol [121°] by tin and HCl (Fischer, *A. Suppl.* 7, 189). Unstable scales; reduces $AgNO_3$, forming a mirror.—B'HCl: ppd. by HCl from solution.—$B'_2H_2SO_4$.

Di-chloro-*p*-amido-phenol

$C_6H_2Cl_2(NH_2)(OH)$ [1:3:5:2]. [167°]. From di-chloro-nitro-phenol [125°] by tin and HCl (Kollrepp, *A.* 234, 10; Seifart, *A. Suppl.* 7, 202). Needles (from water); may be sublimed. Oxidation gives di-chloro-quinone. HCl and bleaching powder give di-chloro-quinonimide.—B'HCl. B'HBr: hexagonal plates; v. sl. sol. cold water.—$B'_2H_2SO_4$ 3aq: needles.—$B'HNO_3$: [110°]; plates.—$B'H_2C_2O_4$: needles.

Di-chloro-*p*-amido-phenol $C_6H_2Cl_2(NH_2)(OH)$. [173°]. Formed by passing HCl into an ethereal solution of *p*-nitroso-phenol (Jaeger, *B.* 8, 895). Needles; may be sublimed. Is perhaps identical with the preceding.

Methyl ether $C_6H_2Cl_2(NH_2)(OMe)$. [72°]. Formed by passing HCl into a solution of *p*-nitroso-phenol in MeOH (J.). Long slender needles (from dilute alcohol).

Ethyl ether. $C_6H_2Cl_2(NH_2)(OEt)$. [46°]. (275°).

Tri-chloro-*m*-amido-phenol

$C_6HCl_3(NH_2)(OH)$ [1:3:5:6:2]. [95°]. Formed from tri-chloro-nitro-phenol $C_6HCl_3(NO_2)(OH)$ by reduction with tin and HCl (Daccomo, *B.* 18, 1166). Colourless silky needles. V. sol. alcohol, ether, benzene, and hot water; Fe_2Cl_6 gives a splendid violet-red colouration.

Tri-chloro-*p*-amido-phenol

$C_6HCl_3(NH_2)(OH)$. [159°].

Formation.—1. From *p*-amido-phenol by chlorination; the by-products are tri- and tetra- chloro-hydro-quinone (Lampert, *J. pr.* [2] 33, 371).—2. From quinone chloro-imide and conc. HCl (Hirsch, *B.* 11, 1981; 13, 1907).

Preparation.—By passing chlorine gas into conc. HCl in which *p*-amido-phenol hydrochloride is suspended. The reaction is ended as soon as a portion of the crystalline product dissolves completely in water and gives, on adding bleaching-powder solution, flocculent tri-chloro-quinone chloro-imide, while the supernatant liquid shows no turbidity (which would be due to oily di-chloro-quinone chloro-imide). The base is precipitated by Na_2CO_3 (R. Schmitt a. M. Andresen, *J. pr.* [2] 24, 426).

Properties.—Glittering needles (from alcohol). Is a weak base, its hydrochloride being decomposed by boiling with water (Hirsch, *B.* 13, 1903).

Reactions.—1. NaOH solution and air convert it into tri-chloro-quinone. 2. By *diazo-reaction* it yields tri-chloro-phenol [54°].—3. *Bleaching-powder* and HCl give tri-chloro-quinone chlorimide. Salts.—B'HCl.—$B'_2H_2SO_4$: small needles.

CHLORO-*p*-AMIDO-PHENOL ν-SULPHONIC ACID $C_6H_3Cl(OH)(NH.SO_3H)$ [1:2:5]. Formed by adding conc. aqueous $NaHSO_3$ to mono- or di-chloro-quinone chlorimide, air being excluded (Kollrepp, *A.* 234, 21). Anhydrous needles (from hot water), which change under water to trimetric prisms (containing 2½aq). Sl. sol. cold water, insol. ether. Reduces boiling Fehling's solution. Gives a silver mirror. Converted by nitrous acid into the diazo- acid $C_6H_3ClN_2SO_4$ 3aq which crystallises in prisms. Salts.—ZnA'_2: trimetric prisms.—NiA'_2. CuA'_2: minute yellowish-brown needles, insol. cold water.

CHLORO-*o*-AMIDO-DIPHENYL $C_{12}H_{10}ClN$ *i.e.* $C_{12}H_8Cl(NH_2)$. [48°]. Formed by reducing *o*-nitro-diphenyl with tin and HCl (Hubner a. Osten, *A.* 209, 349). Long needles (from dilute alcohol); sl. sol. water, v. e. sol. alcohol and ether. Its salts are partially decomposed by water.—B'HCl: laminæ.—$B'_2H_2PtCl_6$: orange tables.—$B'HNO_3$.—$B'_2H_2SO_4$.

Chloro-di-amido-diphenyl

$C_6H_4(NH_2).C_6H_3Cl.NH_2$. Formed by allowing an alcoholic solution of benzene-azo-*p*-chloro-benzene mixed with $SnCl_2$ and a couple of drops of H_2SO_4 to stand in the cold. The base was not isolated in a pure state. The hydrochloride $B''H_2Cl_2$ forms white concentric needles (Mentha a. Heumann, *B.* 19, 2970).

Di-chloro-di-amido-diphenyl

$C_6H_3Cl(NH_2).C_6H_3Cl(NH_2)$. [60°]. Formed by treating *p*-chloro-benzene-azo-*p*-chloro-benzene $C_6H_4Cl.N_2.C_6H_4Cl$ with $SnCl_2$ (Schultz, *B.* 17, 464). Glittering laminæ.—$B'H_2SO_4$.

CHLORO-DI-AMIDO-DI-PHENYL-AMINE-*o*-CARBOXYLIC ACID

$C_6H_2Cl(NH_2)_2.NH.C_6H_4.CO_2H$. [c. 240°]. Formed by reduction of chloro-di-nitro-di-phenyl-amine-*o*-carboxylic acid with tin and HCl (Jourdan, *B.* 18, 1455). Colourless felted needles. Sl. sol. hot water and ether, nearly insol. benzene and ligroin. Fe_2Cl_6 gives a brownish-violet colouration.

DI-CHLORO-TRI-AMIDO-TRI-PHENYL-CARBINOL $C_{19}H_{17}Cl_2N_3O$ *i.e.* $C(OH)(C_6H_3Cl.NH_2)_2(C_6H_4NH_2)$. *Di-chloro-para-*

rosaniline. Formed by heating *p*-toluidine (21 g.), *o*-chloro-toluidine (50 g.) and aqueous arsenic acid (103 g. of 75 p.c.) at 190° (Heumann a. Heidlberg, *B.* 19, 1989). Lustrous green mass. Dyes a much bluer shade than ordinary rosaniline.

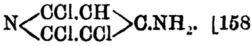
CHLORO-AMIDO-PHENYLENE MERCAPTAN $C_6H_6ClNS_2$ *i.e.* $C_6H_2Cl(NH_2)(SH)_2$ [3:5:2:1]. From the chloride of *m*-chloro-nitro-benzene disulphinic acid by tin and HCl (Allert, *B.* 14, 1436). Does not react with formic acid.

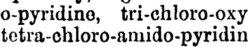
CHLORO-AMIDO-PHENYL-ETHYLENE *v.* CHLORO-AMIDO-STYRENE.

CHLORO - AMIDO - PHENYL - GLYOXYLIC ACID *v.* ISATIN.

CHLORO-AMIDO-PHENYL MERCAPTAN $C_6H_3Cl(NH_2)(SH)$. [130°]. From *m*-chloro-nitro-benzene sulphonic acid, tin, and HCl (Allert, *B.* 14, 1435).—B'HCl.

Exo-**CHLORO**-*eso*-**AMIDO-PROPYL-PYROCATECHIN** *Mono-methyl ether* $C_3H_6Cl.C_6H_2(NH_2)(OMe)(OH)$ [1:5:3:4]. [97°]. From nitro-eugenol $C_3H_5.C_6H_2(NO_2)(OMe)(OH)$ by tin and HCl (Weselsky a. Benedikt, *M.* 3, 389). Pearly plates (from alcohol).—B'HCl aq.

TRI-CHLORO-AMIDO-PYRIDINE $C_5H_3Cl_3N_2$ probably  $N{<}{\begin{smallmatrix}CCl.CH\\CCl.CCl\end{smallmatrix}}{>}C.NH_2$. [158°]. Formed in small quantity, together with di-chloro-di-oxy-amido-pyridine, tri-chloro-oxy-amido-pyridine, and tetra-chloro-amido-pyridine, by heating glutazine with PCl_5 (6 to 7 pts.). Long felted colourless needles. Sublimable. V. sol. alcohol, sl. sol. hot water. Dissolves in aqueous acids, but not in alkalis. Its *bromo-derivative* forms flat colourless needles [223°] (Stokes a. Pechmann, *B.* 19, 2710; *Am.* 8, 392).

Tetra-chloro-amido-pyridine $C_5H_2N_2Cl_4$ probably  $N{<}{\begin{smallmatrix}CCl.CCl\\CCl.CCl\end{smallmatrix}}{>}C.NH_2$. [212°]. Formed, together with an equal quantity of tri-chloro-oxy-amido-pyridine, and small quantities of di-chloro-di-oxy-amido-pyridine and tri-chloro-amido-pyridine, by heating glutazine with PCl_5 (6 to 7 mols.). Thin colourless plates or cubical crystals. Sublimable. Sol. hot benzene, m. sol. hot alcohol, sl. sol. cold alcohol, insol. water. It does not dissolve in aqueous alkalis, and only slightly in conc. HCl. Alcoholic NaOEt forms $C_5H_2N_2Cl_3(OEt)$ [83°] and $C_5H_2N_2Cl_2(OEt)_2$ [98°] (Stokes a. Pechmann, *B.* 19, 2710; *Am.* 8, 396).

DI-CHLORO-DI-AMIDO-QUINONE $C_6Cl_2(NH_2)_2O_2$. *Chloranilamide.* Prepared by adding crystallised tetra-chloro-quinone rubbed up with alcohol to a boiling alcoholic solution of ammonia; after the tetra-chloro-quinone has dissolved, the compound separates in brown needles (Laurent, *Rev. Scient.* 19, 141; *A.* 52, 347; Knapp a. Schultz, *A.* 210, 183). Dark lustrous needles, insol. water, alcohol, and ether; readily sublimed. Its solution in alcoholic KOH is violet. Boiling SnCl$_2$ forms unstable $C_6Cl_2(NH_2)_2(OH)_2$. Fuming HNO_3 forms chloropicrin and oxalic acid.

ω-CHLORO-*o*-AMIDO-STYRENE $C_6H_4(NH_2).CH:CHCl$. *o-Amido-phenyl-ω-chloro-ethylene.* White concentric prisms. V. sol. alcohol and ether, v. sl. sol. cold water. Formed by reduction of ω-chloro-*o*-nitro-styrene with tin and HCl. By heating with sodium ethylate at about 170° it gives indole.—B'HCl: colourless needles, v. sol. water and alcohol (Lipp, *B.* 17, 1071).

CHLORO-AMIDO-SULPHO-BENZOIC ACID $C_7H_6ClNSO_5$ *i.e.* $C_6H_2Cl(NH_2)(SO_3H)(CO_2H)$ [1:2:*x*:3]. From chloro-*o*-amido-benzoic acid and fuming H_2SO_4 (Cunze a. Hübner, *A.* 135, 113).—BaA'': clumps.

CHLORO-AMIDO-THYMOL $C_6HClMePr(NH_2)(OH)$. [101°] (A.); [103°] (S.).

Preparation.—1. By pouring 4 vols. conc. HCl upon thymo-quinone-chloro-imide (*q.v.*); the liquid begins to boil and yellow crystals separate. The liquid is shaken with ether, and the ether, containing chloro-thymo-quinones, is decanted; the residue, in which the chloro-amido-thymol hydrochloride is suspended, is then filtered and decomposed by Na_2CO_3. It dissolves in excess of Na_2CO_3 giving the solution a green colour. This must be avoided.—2. In a similar way from chloro-thymo-quinone-chloro-imide (*q.v.*). 3. From thymo-quinone-oxim (nitroso-thymol) and cold fuming HClAq (Sutkowski, *B.* 19, 2315).

Properties.—Glittering crystals (from water). V. sol. alcohol and ether (Andresen, *J. pr.* [2] 23, 175). Bleaching-powder forms chloro-thymoquinone chlorimide. Heating with chloranil in HOAc produces a red dye $C_{30}H_{35}Cl_3N_2O_3$ [232°].

CHLORO-AMIDO-TOLUENE *v.* CHLORO-TOLUIDINE.

CHLORO-AMIDO-XYLENE *v.* CHLORO-XYLIDINE.

exo-**Chloro-amido-*o*-xylene** $ClCH_2.C_6H_4.CH_2NH_2$. Formed by the action of HClAq at 200° on its phthalyl derivative (Strassmann, *B.* 21, 581).

Phthalyl derivative [1·2]$ClCH_2C_6H_4.CH_2.N(CO)_2C_6H_4$[1·2]. *Exo-chloro-xylene-phthalimide.* [140°]. Formed by the action of exo-di-chloro-*o*-xylene (1 mol.) on potassium phthalimide (1 mol.) at 200° (Strassmann, *B.* 21, 580). Prisms (from alcohol). Heated with HClAq to 200° it is converted into phthalic acid and exo-chloro-amido-xylene.

ω-CHLORO-ISOAMYL ACETATE $C_4H_9.CHCl.OAc$. (118°-128°). S.G. $\frac{17}{}$ ·987. From isovaleric aldehyde and AcCl (Maxwell Simpson, *Pr.* 27, 120). Liquid; slowly decomposed by water.

Tri-chloro-*sec*-amyl-acetate $CHMe(C_3H_4Cl_3).OAc$. (129°–134°) at 25 mm.; (227°) at 726 mm. S.G. $\frac{11.5}{11.5}$ 1·305. From methyl-tri-chloro-propyl carbinol and AcCl (Garzarolli-Thurnlackh, *A.* 223, 151).

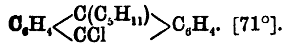
CHLORO-AMYL-ALCOHOL $C_5H_{11}ClO$ *i.e.* $C_5H_{10}Cl(OH)$. *Amylene glycol chlorhydrin.* (155°). From crude amylene and aqueous HClO (Carius, *A.* 126, 199; Eltekoff, *J. R.* 14, 360). V. sol. water. Decomposed by potash with formation of amylene oxide. Na_2SO_3 forms oxy-pentane sulphonic acid (*q. v.*).

Tri-chloro-amyl alcohol $C_5H_9Cl_3O$ *i.e.* $CH_3.CHCl.CCl_2.CHMe.OH$. [50·5°]. (109°) at 20 mm.; (124°) at 41 mm. From tri-chloro-butyric aldehyde and $ZnMe_2$ in ether, followed by water (Garzarolli-Thurnlackh, *A.* 223, 149).

Properties.—Silky needles grouped in rosettes (from ether). Smells of camphor. Volatile with steam. Faintly soluble in water, v. sol. alcohol and ether. Carbonised by conc. H_2SO_4.

Reactions.—1. Warm fuming HNO$_3$ gives CO$_2$ and tri-chloro-butyric acid.—2. H$_2$SO$_4$ and K$_2$Cr$_2$O$_7$ give the ketone C$_3$H$_4$Cl$_3$.CO.Me (191°–193°).—3. Finely divided *iron* and *acetic acid* reduce it to chloro-pentenyl alcohol (*q. v.*).

CHLORO-AMYL-ANTHRACENE C$_{19}$H$_{19}$Cl or



$C_6H_4\!<\!\begin{matrix}C(C_5H_{11})\\CCl\end{matrix}\!>\!C_6H_4$

[71°]. Prepared by chlorination of amyl-anthracene in CHCl$_3$. Light yellow needles with blue fluorescence.

Picric acid compound: red needles (Liebermann a. Tobias, *B.* 14, 797).

α-CHLORO-*n*-AMYLENE C$_5$H$_9$Cl *i.e.* CH$_3$.CH$_2$.CH$_2$.CCl:CH$_2$. (96°). S.G. $^{5\cdot1}$ ·872. From amylene chloride and alcoholic KOH (Bruylants, *B.* 8, 411).

ω-Chloro-iso-amylene (CH$_3$)$_2$CH.CH:CHCl. (86°). From isoamylidene dichloride ^{i}PrCH$_2$.CHCl$_2$ and alcoholic KOH (B.).

Chloro-amylene C$_5$H$_9$Cl. *Valerylene hydrochloride.* (100°). From valerylene and fuming aqueous HCl at 100° (Reboul, *Z.* 1867, 173).

Isoprene hydrochloride C$_5$H$_9$Cl. (85°–91°). S.G. ^{0} ·885 (Bouchardat, *C. R.* 89, 1317).

Di-chloro-amylene CH$_3$.CH CCl.CHCl.CH$_3$. (142°–144°) at 736 mm. From chloro-pentenyl alcohol C$_3$H$_4$Cl.CH(OH).CH$_3$ by PCl$_3$. Partly converted by boiling water into chloro-pentenyl alcohol (Garzarolli-Thurnlackh, *A.* 223, 160).

Di-chloro-amylene C$_5$H$_8$Cl$_2$. (146°). From tri-chloro-hexoic aldehyde and conc. KOHAq (Pinner, *A.* 179, 35; *B.* 10, 1052). Gives with bromine C$_5$H$_8$Cl$_2$Br$_2$ (230°–240°).

Tri-chloro-amylene C$_5$H$_7$Cl$_3$. (200°). From tetra-chloro-pentane (240°) and alcoholic KOH (Bauer, *C. R.* 51, 572).

CHLORO-AMYLENE DI-CARBAMIC ETHER C$_{11}$H$_{21}$ClN$_2$O$_4$ *i.e.* C$_5$H$_9$Cl(NH.CO$_2$Et)$_2$. [130°]. From isovaleric aldehyde, carbamic ether, and HCl (Bischoff, *B.* 7, 633).

CHLORO-DI-AMYL SULPHONE C$_5$H$_{10}$Cl.SO$_2$.C$_5$H$_{11}$. (330°). Formed together with di-chloro-di-amyl sulphone (C$_5$H$_{10}$Cl)$_2$SO$_2$ by treating di-amyl sulphone with ICl$_3$ at 130° (Spring a. Winssinger, *Bl.* [2] 41, 307).

CHLORO-ANETHOL C$_{10}$H$_{11}$ClO. [6°]. (258°) (Ladenburg); (229°) (Landolph). S.G. ^{0} 1·115 (Lad.); ^{20} 1·191 (Lan.). Prepared by the action of PCl$_5$ on anethol (Ladenburg, *A. Suppl.* 8, 90). By treatment with KOH it gives a mixture of two liquids, the first of which, C$_{16}$H$_{20}$O$_3$, boils at (268°–270°), and the second can be converted into the first by more prolonged action of the KOH (Landolph, *B.* 13, 148).

CHLORO-ANGELIC ACID CH$_3$.CCl:CH.CH$_2$.CO$_2$H (?) [104°]. The ethyl ether is formed by treating di-chloro-angelic acid in alcoholic solution with zinc and HCl (Pinner a. Klein, *B.* 11, 1498).

Ethyl ether EtA′. Liquid.

Isomeride *v.* Chloro-tiglic acid.

Di-chloro-angelic acid C$_5$H$_6$Cl$_2$O$_2$ *i.e.* CH$_3$.CCl:CH.CHCl.CO$_2$H(?). From chloro-oxy-angelic acid and PCl$_5$ (Pinner a. Klein, *B.* 11, 1498). Oil.

CHLORANILIC ACID *v.* *p*-Di-chloro-*p*-di-oxy-quinone.

***o*-CHLORO-ANILINE** C$_6$H$_6$ClN *i.e.* C$_6$H$_4$Cl(NH$_2$) [1:2]. Mol. w. 127½. (207° i. V.). S.G. ^{0} 1·2338.

Formation.—By reduction of *o*-chloro-nitro-benzene. May be separated from *p*-chloro-aniline by distilling the sulphates with steam, that of *o*-chloro-aniline being decomposed (Beilstein a. Kurbatoff, *A.* 176, 27).

Salts.—B′HCl: trimetric plates: S. 12 at 15°.—B′HNO$_3$: S. 10 at 13·5°.—Picrate: v. sl. sol. cold water; sl. sol. alcohol.

Acetyl derivative C$_6$H$_4$Cl(NHAc). [88°]. Long flat needles (from dilute HOAc) (Beilstein a. Kurbatoff, *A.* 182, 100).

***m*-Chloro-aniline** C$_6$H$_4$Cl(NH$_2$) [1:3]. (230° i. V.). S.G. ^{0} 1·243. From *m*-chloro-nitro-benzene (B. a. K.). Its salts are hardly decomposed by boiling water.—B′HCl.—B′HBr: long red needles (Staedel, *B.* 16, 28).—B′HNO$_3$.—B′$_2$H$_2$SO$_4$: sl. sol. cold water.

Acetyl derivative C$_6$H$_4$Cl(NHAc). [73°]. Needles.

***p*-Chloro-aniline** C$_6$H$_4$Cl(NH$_2$) [1:4]. [70°]. (231° i. V.).

Formation.—1. By distilling chloro-isatin with KOH (Hofmann, *A.* 53, 1).—2. By reducing *p*-chloro-nitro-benzene with SnCl$_2$.—3. From its acetyl derivative obtained by chlorinating acetanilide (Mills, *P. M.* 49, 21).

Properties.—Trimetric prisms. **Is a strong base.**

Salts.—B′HCl.—B′$_2$H$_2$PtCl$_6$.—B′HNO$_3$: laminæ, S. 6·7 at 12·5°. B′$_2$H$_2$SO$_4$: sl. sol. cold water.—B′H$_2$C$_2$O$_4$ ½aq.

Acetyl derivative C$_6$H$_4$Cl.NHAc. [173°]. Thick needles (from dilute HOAc).

***c*-Di-chloro-aniline** C$_6$H$_3$Cl$_2$(NH$_2$) [1:2:3]. Mol. w. 162. [24°]. (252°). From nitro-benzene by chlorination, in presence of SbCl$_5$ and reduction (Beilstein a. Kurbatoff, *A.* 196, 214; *B.* 11, 1860). Needles (from ligroin).

Acetyl derivative C$_6$H$_3$Cl$_2$(NHAc). [157°].

***c*-Di-chloro-aniline** C$_6$H$_3$Cl$_2$(NH$_2$) [3:1:2]. [39°]. From di-chloro-nitro-benzene [71°] (B. a. K.). Needles, v. sol. ligroin.

Acetyl derivative C$_6$H$_3$Cl$_2$(NHAc). [175°].

***s*-Di-chloro-aniline** C$_6$H$_3$Cl$_2$(NH$_2$) [1:3:5]. [50·5°]. (260° i. V.). From *s*-di-chloro-nitro-benzene (Witt, *B.* 8, 145; B. a. K.; Langer, *A.* 215, 120).

Acetyl derivative C$_6$H$_3$Cl$_2$(NHAc). [187°].

Di-chloro-aniline C$_6$H$_3$Cl$_2$(NH$_2$) [1:4:2]. [50°]. (251°). From di-chloro-nitro-benzene [55°] (Jungfleisch, *A. Ch.* [4] 15, 252; B. a. K.). (251°). Formed also by chlorinating *m*-chloro-aniline and by heating nitro-benzene with fuming HCl at 245° (Baumhauer, *A. Suppl.* 7, 209). CrO$_3$ gives di-chloro-quinone.

Acetyl derivative C$_6$H$_3$Cl$_2$(NHAc). [132°].

Di-chloro-aniline C$_6$H$_3$Cl$_2$(NH$_2$) [1:3:4]. [63°]. (245°). From acetanilide (1 mol.) and chlorine (2 mols.). Obtained also by chlorinating *o*- or *p*-chloro-aniline (Griess, *A.* 121, 268; Beilstein. *A.* 182, 95; Witt, *B.* 7, 1602).—B′HCl.—B′$_2$H$_2$PtCl$_6$.

Acetyl derivative C$_6$H$_3$Cl$_2$(NHAc). [143°]

Di-chloro-aniline C$_6$H$_3$Cl$_2$(NH$_2$) [1:2:4] [71·5°]. (272°). From di-chloro-nitro-benzene [43°], or by chlorinating *m*-chloro-aniline (B. a. K.). Long needles; strong base.

Acetyl derivative C$_6$H$_3$Cl$_2$(NHAc) [120·5°].

***c*-Tri-chloro-aniline** C$_6$H$_2$Cl$_3$(NH$_2$) [1:2:3:4] Mol. w. 196·5. [67·5°]. (292° i. V.).

Formation. –1. From its acetyl derivative. 2 By reducing $C_6H_2(NO_2)Cl_3$ [1:2:3:4].

Acetyl derivative $C_6H_2(NHAc)Cl_3$. [122°]. When chlorine is passed into a solution of acetyl *m*-chloro-aniline in strong (90 p.c.) acetic acid, two acetyl-trichloro-anilines are formed; one of these, $C_6H_2Cl_3(NHAc)$ [1:2:4:5] [185°] is hardly soluble in dilute (50 p.c.) acetic acid, the other [1:2:3:4] is soluble (Beilstein a. Kurbatoff, *A.* 192, 234).

Tri-chloro-aniline $C_6H_2Cl_3(NH_2)$ [1:3:5:6]. [77·5°]. (262° i. V.). From aniline, *p*-chloro-aniline, or (1, 3, 4)-di-chloro-aniline in glacial acetic acid by chlorine (Hofmann, *A.* 53, 35; Beilstein a. Kurbatoff, *B.* 11, 1862; Langer, *A.* 215, 114). Also from aniline and SO_2Cl_2 (Wenghöffer, *J. pr.* [2] 16, 449). Long needles (from ligroin).

Acetyl derivative $C_6H_2Cl_3(NH_2)$. [204°].

Tri-chloro-aniline $C_6H_2Cl_3(NH_2)$ [1:2:4:5]. [96°]. From $C_6H_2(NO_2)Cl_3$ [58°] (Lesimple, *A.* 137, 125; Beilstein a. Kurbatoff, *A.* 192, 231). Obtained also by chlorinating (2, 5, 1)- or (3, 4, 1)-di-chloro-aniline, or *m*-chloro-aniline. Needles (from ligroin).

Acetyl derivative $C_6H_2Cl_3(NHAc)$. [185°].

***i*-Tetra-chloro-aniline** $C_6HCl_4(NH_2)$ [1:2:3:5:6]. [88°]. Formed by chlorinating *m*-chloro-aniline (B. a. K.). Gives, by eliminating NH_2, tetra-chloro-benzene [51°].

Acetyl derivative $C_6HCl_4(NHAc)$ [174°].

***s*-Tetra-chloro-aniline** $C_6HCl_4(NH_2)$ [1:2:4:5:6]. [90°]. Prepared by reducing *s*-tetra-chloro-nitro-benzene (Lesimple, *Z.* 1868, 227).

***c*-Tetra-chloro-aniline** $C_6HCl_4(NH_2)$. [118°]. From *c*-tetra-chloro-nitro-benzene (Beilstein a. Kurbatoff, *B.* 11, 1862).

Acetyl derivative [154°] (Tust, *B.* 21, 1533).

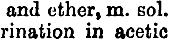
Penta-chloro-aniline $C_6Cl_5NH_2$ [232°]. From *s*-di-chloro-aniline by chlorinating it in ethereal solution (Langer, *A.* 215, 120). Obtained also by reducing penta-chloro-nitro-benzene (Jungfleisch). Long white needles (from alcohol). V. sol. alcohol and ether, m. sol. benzoline. By further chlorination in acetic acid solution it gives penta-chloro-phenyl hypochlorite C_6Cl_5OCl.

CHLORO-ANISIC-ACID *v. Methyl derivative* of CHLORO-OXY-BENZOIC ACID.

CHLORO-ANISIDINE *v. Methyl ether* of CHLORO-AMIDO-PHENOL.

CHLORO-ANTHRACENE $C_{14}H_9Cl$. [103°]. Obtained by fusing anthracene dichloride (Perkin, *C. N.* 34, 145). Golden-yellow needles, v. sol. ether, alcohol, and benzene. The picric acid compound forms scarlet needles.

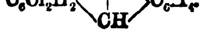
Di-(*A*)-chloro-anthracene



$C_6H_4\left<\begin{matrix}CCl\\CCl\end{matrix}\right>C_6H_4$.

[209°]. Formed by the action of (2 mols. of) chlorine upon anthracene-(*A*)-carboxylic acid or upon (*A*. 1)-chloro-anthracene-(*A*. 2)-carboxylic acid (Behla, *B.* 20, 704). Prepared by chlorinating anthracene (Laurent, *A.* 34, 294; Perkin, *C. J.* 24, 14; Græbe a. Liebermann, *A.* 160, 137; *Suppl.* 7, 284). Long yellow needles; v. sol. benzene, sl. sol. alcohol and ether. Not affected by boiling KOH. Gives anthraquinone on oxidation.

Di-chloro-anthracene

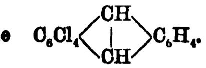


$C_6Cl_2H_2\left<\begin{matrix}CH\\|\\CH\end{matrix}\right>C_6H_4$.

[255°]. From tetra-chloro-anthraquinone by heating with zinc-dust and aqueous ammonia (Kircher, *A.* 238, 347; *B.* 17, 1169). Slender needles. On oxidation it gives di-chloro-anthraquinone.

Tri-chloro-anthracene $C_{14}H_7Cl_3$. [163°]. From di-chloro-anthracene dichloride and alcoholic KOH (Schwarzer, *B.* 10, 378; *cf.* G. a. L.). Long golden needles (from alcohol). The alcoholic solution shows blue fluorescence.

Tetra-chloro-anthracene



$C_6Cl_4\left<\begin{matrix}CH\\|\\CH\end{matrix}\right>C_6H_4$.

[149°]. From tetra-chloro-benzoyl-benzoic acid (1 pt.), red phosphorus ($\frac{1}{2}$ pt.), and fuming HI ($4\frac{1}{2}$ pts.) at 215° (Kircher, *A.* 238, 346). Slender needles, sol. benzene and chloroform. CrO_3 gives the corresponding tetra-chloro-anthraquinone.

Tetra-chloro-anthracene $C_{14}H_6Cl_4$. [152°]. Prepared by the action of boiling alcoholic KOH on the di-chloro-anthracene tetrachloride [206°] obtained from nitroso-anthrone and PCl_5 (Liebermann a. Lindermann, *B.* 13, 1589). Yellow needles, sol. hot acetic acid, sl. sol. alcohol. On oxidation with CrO_3 it gives crystalline dichlor-anthraquinone.

Tetra-chloro-anthracene $C_{14}H_4Cl_4$. [164°] (H.); [220°] (G. a. L.). Formed by the action of alcoholic KOH upon pure di-chloro-anthracene tetra-chloride [187°] (Hammerschlag, *B.* 19, 1108; Græbe a. Liebermann, *A. Suppl.* 7, 283). Golden yellow needles. Sl. sol. nearly all solvents. By CrO_3 and acetic acid it is oxidised to di-chloro-anthraquinone [205°].

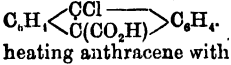
Hexa-chloro-anthracene $C_{14}H_4Cl_6$. [320°-330°]. Yellow needles. Prepared by the action of $SbCl_5$ on di-chloro-anthracene dichloride. Oxidation with $K_2Cr_2O_7$ and H_2SO_4 gives tetra-chloro-anthraquinone (Bolas, *C. N.* 28, 167; Diehl, *B.* 11, 175).

Hepta-chloro-anthracene $C_{14}H_3Cl_7$. [above 350°]. Prepared by the prolonged action of $SbCl_5$ on di-chloro-anthracene-dichloride at 260°. Sublimes in yellow needles (Diehl, *B.* 11, 176).

Octo-chloro-anthracene $C_{14}H_2Cl_8$. [above 350°]. Feathery crystals. Prepared by the prolonged action of $SbCl_5$ at 280° on the lower chlorinated anthracenes (Diehl, *B.* 11, 177). Ruoff (*B.* 9, 1488) could only obtain hexa-chloro-benzene.

DI-CHLORO-ANTHRACENE TETRA-BROMIDE $C_{10}H_8Cl_2Br_4$. [166°] (S.); [178°] (Hammerschlag, *B.* 19, 1106). Obtained by exposing di-chloro-anthracene [209°] to bromine-vapour for a considerable time (G. a. L.; Schwarzer, *B.* 10, 376). Satiny needles (from benzene); sl. sol. alcohol and ether; v. sol. benzene and $CHCl_3$. At 180°–190° it is converted into di-chloro-bromo-anthracene [168°]. Boiling alcoholic KOH gives di-chloro-di-bromo-anthracene.

(*A.* 1)-CHLORO-ANTHRACENE-(*A.* 2)-CARBOXYLIC ACID $C_{15}H_9O_2Cl$ *i.e.*

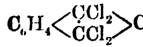


$C_6H_4\left<\begin{matrix}CCl\\C(CO_2H)\end{matrix}\right>C_6H_4$.

[259°]. Obtained by heating anthracene with carbonyl chloride under pressure at 240°–250°; or by passing chlorine (1 mol.) into a solution of anthracene-(*A*)-carboxylic acid in $CHCl_3$. Long yellow glistening needles. Sublimes. Sol. alcohol, ether, and acetic acid; sl. sol. benzene, chloroform, and xylene; v. sl. sol. water and ligroin. Its solutions have a blue fluorescence. At its melting-point it evolves CO_2, leaving (*A*)-chloro-anthracene. By CrO_3, $KMnO_4$, or dilute HNO_3 it is oxidised to anthraquinone. Alcoholic KOH at 160°-170° reduces it to anthracene-(*A*)-carboxylic acid. Chlorine converts it into di-(*A*)-chloro-anthracene. Salts.—KA′: very slender yellow needles.—AgA′: minute yellow prisms.—BaA'_2: thick yellowish glistening prisms (from water) or needles (from alcohol).

Methyl ether MeA′: [123°]; yellow needles or large six-sided tables; sol. alcohol, ether, &c., with a blue fluorescence; insol. water (Behla, *B.* 20, 701).

DI-CHLORO-ANTHRACENE DI-CHLORIDE



$C_6H_4<\begin{matrix}CCl_2\\CCl_2\end{matrix}>C_6H_4$. [150°]. Formed by passing chlorine into anthracene dissolved in chloroform (Schwarzer, *B.* 10, 377). Prisms (from chloroform); sl. sol. alcohol and ether, v. sol. benzene. At 170° it yields tri-chloro-anthracene [163°]. Boiling alcoholic KOH converts it into anthraquinone.

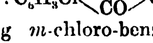
Di-chloro-anthracene-tetra-chloride $C_{14}H_8Cl_6$. [187°] (H.); [145°] (D.). Thin white needles. Prepared by passing chlorine for a long time through a benzene solution of anthracene or dichloranthracene [209°]. By treatment with alcoholic KOH it yields tetra-chloro-anthracene [164°] (Hammerschlag, *B.* 19, 1107; *cf.* Diehl, *B.* 11, 174).

Di-chloro-anthracene-tetrachloride $C_{14}H_8Cl_2.Cl_4$. [205°-207°]. White needles. Does not fluoresce. Prepared by heating nitroso-anthrone with PCl_5 to 180°. By boiling with alcoholic KOH it gives tetra-chloro-anthracene [152°]. (Liebermann a. Lindermann, *B.* 13, 1588).

DI-CHLORO-ANTHRACENE DISULPHONIC ACID $C_{14}H_6Cl_2(SO_3H)_2$. From (1 pt.) di-chloro-anthracene [209°] and (5 pts.) fuming H_2SO_4 at 100° (Perkin, *C. J.* 24, 15). Orange needles; v. sol. water but ppd. by HCl or H_2SO_4. Dilute solutions of the acid and its salts fluoresce blue. On oxidation it gives anthraquinone disulphonic acid. Na_2A''*x* aq.—BaA″.—SrA″.

CHLORO-ANTHRANILIC ACID *v.* CHLORO-AMIDO-BENZOIC ACID.

***m*-CHLORO-ANTHRAQUINONE** $C_{14}H_7ClO_2$ *i.e.*



$C_6H_3Cl<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$. [204°]. Formed by heating *m*-chloro-benzoyl-benzoic acid with sulphuric acid at 160°-175°. Yellowish-grey needles; v. sol. hot C_6H_6, sl. sol. acetic acid CS_2, and hot alcohol. Sublimes without decomposition (Graebe a. Rée, *C. J.* 49, 531)

Di-chloro-anthraquinone $C_6H_4(C_2O_2)C_6H_2Cl_2$. [205°]. Formed by oxidation of tetra-chloro-anthracene [164°] with CrO_3 and acetic acid (Hammerschlag, *B.* 19, 1109; *cf.* Graebe a. Liebermann, *A. Suppl.* 7, 290). Formed also by heating anthracene with $SbCl_5$ at 100° (Diehl, *B.* 11, 179). Glistening golden needles (from acetic acid). By NaOH fusion it gives alizarin.

Di-chloro-anthraquinone $C_6Cl_2H_2(C_2O_2)C_6H_4$. [261°]. Formed by oxidising di-chloro-anthracene [255°]. Needles (from chloroform-alcohol). Gives alizarin when fused with potash (Kircher, *B.* 17, 1169).

Tri-chloro-anthraquinone $C_{14}H_5Cl_3O_2$ [284°-290°]. Got by heating anthraquinone with $SbCl_5$ at 180° (Diehl, *B.* 11, 180). Yellow needles.

Tetra-chloro-anthraquinone $C_6Cl_4(C_2O_2)C_6H_4$. [191°]. From tetra-chloro-*o*-benzoyl-benzoic acid and H_2SO_4 at 100° (Kircher, *A.* 238, 344; *B.* 17, 1167). Golden needles (from benzene-alcohol). Oxidised by fuming HNO_3 at 140° giving tetra-chlorophthalic acid. Reduced by distillation with zinc-dust to anthracene. Yields phthalic acid on fusion with NaOH.

Di-sulphonic acid *$C_{14}H_2Cl_4O_2(SO_3H)_2$. Salts.—BaA″.—CaA″.

Tetra-chloro-anthraquinone $C_{14}H_4Cl_4O_2$. [320°-330°]. Prepared by long heating of di-chloro-anthraquinone with 6 pts. of $SbCl_5$ at 200° (Diehl, *B.* 11, 180). Yellow needles

Penta-chloro-anthraquinone $C_{14}H_3Cl_5O_2$. Prepared by heating di-chloro-anthraquinone with 8 pts. $SbCl_5$ at 250° (D.). Sublimes without melting. Insoluble in the ordinary solvents.

CHLORO-ATROPIC ACID $C_9H_7ClO_2$. [85°]. From tropic acid and PCl_5. Needles (Ladenburg, *B.* 12, 948).

CHLORO-AZO-BENZENE *v.* BENZENE-AZO-CHLORO-BENZENE, vol. i. p. 374.

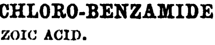
Di-chloro-azo-benzene *v.* CHLORO-BENZENE AZO-CHLORO-BENZENE, vol. i. p. 381.

CHLORO-AZOPHENINE $C_{30}H_{23}ClN_4$. [230°]. Formed by heating *p*-chloro-*p*-nitroso-di-phenyl-amine with aniline and aniline hydrochloride at 100°. Very similar to azophenine, but more sol. benzene (O. Fischer a. Hepp, *B.* 20, 2481).

Tri-chloro-azophenine $C_{30}H_{21}Cl_3N$. [246°] (Fischer a. Hepp, *B.* 21, 676).

TRI-CHLORO-AZO-PHENOL *v.* OXY-BENZENE-AZO-PHENOL, vol. i. p. 388.

DI-CHLORO-BARBITURIC ACID $C_4H_2Cl_2N_2O_3$ *i. e.*



$CCl_2<\begin{matrix}CO.NH\\CO.NH\end{matrix}>CO$. Formed by oxidising di-chloro-oxy-methyl-uracil with fuming HNO_3 (Behrend, *A.* 236, 64). Trimetric crystals, *a*:*b*:*c* = ·777:1: ·893. V. e. sol. alcohol and ether; sol. water.

CHLORO-BENZALDEHYDE *v.* CHLORO-BENZOIC ALDEHYDE.

CHLORO-ISOBENZALPHTHALIMIDINE *v.* CHLORO-OXY-PHENYL-ISOQUINOLINE.

CHLORO-BENZAMIDE *v.* *Amide* of CHLORO-BENZOIC ACID.

CHLORO-BENZENE C_6H_5Cl. Mol. w. 112½. [-40°]. (132°). S.G. $^{20}_{4}$ 1·1066. μ_β 1·5369. R_∞ 50·67 (Bruhl). H.F.p. -11,220. H.F.v.—12,380 (Th.). S.H. (7°-64°) ·326 (Schiff, *G.* 17, 486). *Vapour-pressure*, Ramsay a. Young (*C. J.* 47, 654). S.V. 114·3 (Schiff, *A.* 220, 98); 114·5 (Ramsay).

Formation.—1. From phenol and PCl_5 (Laurent a. Gerhardt, *A.* 75, 79; Williamson a. Scrugham, *C. J.* 7, 238; Riche, *A.* 121, 357).—2. By the action of chlorine on benzene in presence of iodine or other carriers (Hugo Muller, *C. J.* 15, 41; Fittig, *A.* 133, 49).—3. From benzene and SO_2Cl_2 at 150° (Dumas, *Z.* 1866, 705). 4. From S_2Cl_2 and benzene at 250° (Schmidt, *B.* 11, 1173).—5. By heating benzene sulpho-chloride with PCl_5 at 210° (Barbaglia a. Kekulé, *B.* 5, 875).—6. A solution of diazobenzene chloride, prepared from 30 grms. of aniline, and a large excess of HCl is slowly run into a nearly boiling solution of Cu_2Cl_2 in HCl (150 grms. of a 10-p.c. solution of Cu_2Cl_2). The bromo-benzene is distilled off with steam (Sandmeyer, *B.* 17, 1633).—7. By heating diazobenzene with a large excess of strong HCl; the yield is 40 p.c. of the theoretical (Gasiorowski a. Waÿss, *B.* 18, 1936).

Properties.—Colourless liquid. When led through a red-hot tube it forms diphenyl, chloro-diphenyl, di-chloro-diphenyl, and di-phenyl-benzene (Kramers, *A.* 189, 135). Not affected by boiling with Al_2Cl_6. Converted by sodium into diphenyl. MnO_2 and H_2SO_4 give formic and *p*-chloro-benzoic acid (Carius, *Z.* [2] 4, 505; C. Muller, *Z.* [2] 5, 137). Chloro-benzene passes out of the system as chloro-phenyl-mercapturic acid $C_{12}H_{12}ClNSO_3$.

o-**Di-chloro-benzene** $C_6H_4Cl_2$ [1:2]. Mol. w. 147. (179° i. V.). S.G. ^{0} 1·328 (B. a. K.); 1·325 (F. a. C.).

Formation.—1. In small quantity, by chlorinating benzene (Beilstein a. Kurbatoff, *A.* 176, 42; 182, 94; *B.* 7, 1398, 1759). Separated from the greater part of the solid *p*-di-chloro-benzene by pressure; it is then heated with fuming H_2SO_4 at 210° for 2 days; this sulphonates only *o*-di-chloro-benzene. The resulting sulphonic acid is purified by crystallisation, and reconverted into di-chloro-benzene by hydrolysis (Friedel a. Crafts, *A. Ch.* [6] 10, 411).—2. From *o*-chloro-phenol and PCl_5 (B. a. K.).

Properties.—Liquid. Gives a nitro- derivative [43°]. MeCl and Al_2Cl_6 at 100° give chiefly hexa-methyl-benzene and tri-chloro-mesitylene (F. a. C.).

m-**Di-chloro-benzene** $C_6H_4Cl_2$ [1:3]. (168° uncorr.) (S.); (172°) (K.). S.G ^{0} 1·307.

Formation.—1. By running an aqueous solution of $NaNO_2$ into a hot solution of *m*-phenylene-diamine and Cu_2Cl_2 in dilute HCl (Sandmeyer, *B.* 17, 2652).—2. From di-chloro-aniline by removing NH_2 by the diazo- reaction (Körner, *G.* 4, 341; B. a. K.).—3. From *m*-di-nitro-benzene *viâ* *m*-nitro-aniline, *m*-chloro-nitro-benzene, and *m*-chloro-aniline (Griess, *P. T.* 1864 [3] 705).

Properties.—Liquid. HNO_3 (S.G. 1·4) gives a nitro-compound [32°].

p-**Di-chloro-benzene** $C_6H_4Cl_2$ [1:4]. [55°]. (173°). S.G. $^{20\cdot5}$ 1·458; ^{63} 1·211 (Jungfleisch, *A. Ch.* [4] 14, 186). S.V.S. 117·4 (Schiff).

Formation.—1. By running a solution of $NaNO_2$ into a hot solution of *p*-phenylene-diamine and Cu_2Cl_2 in dilute HCl (Sandmeyer, *B.* 17, 2652).—2. The chief product of the action of chlorine (2 mols.) on benzene (1 mol.) in presence of iodine (Hugo Müller, *C. J.* 15, 41; *Z.* 1864, 401; Kõrner, *G.* 4, 324) or in presence of $MoCl_5$ (Aronheim, *B.* 8, 1400).—3. By the action of PCl_5 on phenol *p*-sulphonic acid (Kekulé, *B.* 6, 944) or on *p*-chloro-phenol (Beilstein a. Kurbatoff, *A.* 176, 32; *B.* 7, 1395, 1759).

Properties.—Monoclinic laminæ (from alcohol). Sublimes at ordinary temperatures. Fuming HNO_3 gives a nitro- derivative [55°].

u-**Tri-chloro-benzene** $C_6H_3Cl_3$ [1:3:4]. Mol. w. 181½. [16°]. (213° i. V.). S.G. (of liquid) ^{12} 1·465.

Formation.—1. By chlorination of benzene in presence of iodine (Jungfleisch, *A. Ch.* [4] 15, 264).—2. From di-chloro-aniline, $C_6H_3(NH_2)Cl_2$ [1:3:4] or [1:2:4] displacing NH_2 by Cl by means of the diazo- reaction.—3. From di-chloro-phenol [43°] and PCl_5 (Beilstein a. Kurbatoff, *A.* 192, 230; *B.* 10, 270).—4. From (*β*)-benzene hexa-chloride and alcoholic KOH.

Properties.—Gives on nitration a nitro- derivative [58°].

c-**Tri-chloro-benzene** $C_6H_3Cl_3$ [1:2:3]. [54°]. (219°). By eliminating NH_2 from $C_6H_2(NH_2)Cl_3$ [1:2.3:4] by diazo- reaction (Beilstein a. Kurbatoff, *A.* 192, 235). Also from (1,2,3)-di-chloro-aniline by displacing NH_2 by Cl. V. sol. CS_2 and benzene, sl. sol. alcohol. Gives a nitro- derivative [56°].

s-**Tri-chloro-benzene** $C_6H_3Cl_3$ [1:3:5]. [63·5°]. (208·5° i. V.). From ordinary tri-chloro-aniline, by eliminating NH_2 by diazo- reaction (Körner). Also from chloro-benzene tetra-chloride, and alcoholic KOH (Jungfleisch). V. sol. ether, benzene, CS_2 and light petroleum. Sol. cold alcohol and dilute (50 p.c.) acetic acid. Gives on nitration a nitro- derivative [68°] (B. a. K.), or, when fuming HNO_3 is used, a di-nitro- derivative [130°] (Jackson a. Wing, *Am.* 9, 348).

c-**Tetra-chloro-benzene** $C_6H_2Cl_4$ [1:2:3:4]. Mol. w. 216. [46°]. (254° i. V.). From tri-chloro-aniline $C_6H_2Cl_3(NH_2)$ [1:2:3:4] or [1:3:6:2] by the diazo- reaction (Beilstein a. Kurbatoff, *A.* 192, 238). Long needles (from alcohol). Sl. sol. alcohol, v. sol. ether, light petroleum, CS_2, and strong (90 per cent.) acetic acid. Gives a nitro-derivative [65°].

i-**Tetra-chloro-benzene** $C_6H_2Cl_4$ [1:3:4:5] [51°] (B. a. K.); [35°] (I.). (246° i. V.). From ordinary tri-chloro-aniline displacing NH_2 by Cl by the diazo- reaction (Beilstein a. Kurbatoff, *A.* 192, 238). Obtained also by chlorinating benzene in sunlight (Istrati, *A. Ch.* [6] 6, 383). Colourless needles (from alcohol). Sl. sol. cold alcohol, sol. benzene, v. sol. CS_2 or light petroleum. HNO_3 (S.G. 1·54) gives a nitro- derivative [30°] (Jungfleisch, *A. Ch.* [4] 15, 204), or [22°] (B. a. K.).

s-**Tetra-chloro-benzene** $C_6H_2Cl_4$ [1:2:4:5]. [138°] (245° i. V.) (B.). S.G. ^{10} 1·734; ^{142} 1·399.

Formation.—1. By chlorination of benzene (Jungfleisch).—2. From $C_6H_2Cl_3(NO_2)$ [1:2:3:4] by reduction followed by the diazo- reaction (Beilstein a. Kurbatoff, *A.* 192, 236). 3. In small quantity by the action of chlorine on boiling tri-chloro-toluene (Beilstein a. Kuhlberg, *A.* 152, 247).—4. By the action of Fe_2Cl_6 upon (2, 4, 6, 1)-tri-chloro-phenol (Daccomo, *B.* 18, 1163).

Properties.—Crystallises best from benzene. Sl. sol. alcohol or light petroleum. Fuming HNO_3 forms, besides the nitro- compound [98°], tetra-chloro-quinone. This is the only tetra-chloro-benzene which gives chloranil under these circumstances.

Penta-chloro-benzene C_6HCl_5. [86°]. (276°) (Ladenburg, *A.* 172, 344). S.G. ^{10} 1·842. Formed by chlorinating benzene (J.), di-phenyl sulphone (Otto a. Ostrop, *A.* 141, 93; 154, 182) or tetra-chloro-benzyl chloride (Beilstein a. Kuhlberg, *A.* 152, 247). Slender needles (from alcohol); v. sl. sol. cold alcohol, v. sol. ether and CS_2. After heating for a long time with conc. or fuming H_2SO_4, on pouring the liquid into water a chest-nut-brown pp. containing no sulphur and 36·8 p.c. chlorine is formed; it is called ‘franceine’ by Istrati (*Bl.* [2] 48, 35); it is a red dye, and forms a red solution in alcohol.

Hexa-chloro-benzene C_6Cl_6. Mol. w. 285. [226°]. (326°). S.G. ^{230} 1·569.

Formation.—1. From methylene chloride and ICl or ICl_3 (Höland, *A.* 240, 234).—2. By passing chloroform, CCl_4, or C_2Cl_4 through a red hot tube (Julin; Regnault, *A.* 30, 350; Basset, *C. J.* **20, 443**; Berthelot a. Jungfleisch, *Z.* [2] 4, 565).—**3.** By chlorinating benzene in presence of $SbCl_5$ (Hugo Müller, *Z.* 1864, 40).—4. From tetrachloro-quinone (chloranil) and PCl_5 (Græbe, *A.* 146, 1).—5. Is the ultimate product of the action of $SbCl_5$ with chlorine on all chloro-toluenes and chloro-xylenes (Beilstein a. Kuhlberg, *Z.* [2] 5, 183; *A.* 150, 309).—6. By the action of chlorine in presence of ICl upon all aromatic hydrocarbons, as well as upon aniline, phenol, thymol, camphor (Ruoff, *B.* 9, 1483; 10, 1234); *sec*-hexyl iodide (Krafft, *B.* 9, 1085); and hexachloro-acetone (Cloez, *A. Ch.* [6] 9, 145).

Properties.—Thin prisms (from alcohol-benzene), v. sl. sol. boiling alcohol, sl. sol. ether, m. sol. benzene. When heated with glycerin and NaOH it gives penta-chloro-phenol.

CHLORO-BENZENE-AZO- *v.* AZO-COMPOUNDS.

CHLORO-BENZENE HEXA-CHLORIDE $C_6H_5Cl_7$. [257°]. From di-phenyl sulphone and chlorine in sunlight (Otto, *A.* 141, 101). Small dimetric prisms (from alcohol); v. sl. sol. ether, sl. sol. hot alcohol.

Di-chloro-benzene hexa-chloride $C_6H_4Cl_8$. [above 250°]. From chloro-benzene and chlorine in sunlight (Jungfleisch, *Z.* [2] 4, 486). Prisms (from chloroform); converted into penta-chloro-benzene by boiling alcoholic KOH.

Tri-chloro-benzene hexa-chloride $Cl_6C_6H_3Cl_3$ [1:2:4]. [96°]. Formed by chlorination of benzene (Willgerodt, *J. pr.* [2] 35, 415). Smells of rotten straw. V. e. sol. ether, v. sol. alcohol. Alcoholic KOH converts it into C_6Cl_6 [226°].

CHLORO-BENZENE SULPHINIC ACID $C_6H_4Cl.SO_2H$. [90°]. From chloro-benzene (*p*?)-sulpho-chloride and sodium-amalgam (Otto a. Brummer, *A.* 143, 113; 145, 323; 146, 213). Small needles or long thin columns; sl. sol. cold water. Reduced by Zn and H_2SO_4 to chloro-phenyl mercaptan, and by sodium-amalgam to benzene sulphinic acid. Oxidation gives chloro-benzene sulphonic acid.

Salts.—NaA'_2 2aq.—CaA'_2.—BaA'_2.—PbA'_2.

Ethyl ether EtA'. [123°]. Needles.

CHLORO-BENZENE *o*-SULPHONIC ACID $C_6H_5ClSO_3$ *i.e.* $C_6H_4Cl(SO_3H)$ [1:2]. From amido-benzene *o*-sulphonic acid by displacement of NH_2 by Cl by means of the diazo-reaction (Bahlmann, *A.* 186, 325).

Chloride $C_6H_4Cl.SO_2Cl$ [29°].

Amide $C_6H_4Cl.SO_2NH_2$ [188°].

Chloro-benzene *m*-sulphonic acid $C_6H_4Cl(SO_3H)$ [1:3]. Prepared similarly from amido-benzene *m*-sulphonic acid (Kieselinsky, *A.* 180, 108). Deliquescent plates.—AgA'.—KA'.—CaA'_2.—BaA'_2 2aq.—CuA'_2 5aq.

Chloride $C_6H_4Cl(SO_2Cl)$. Oil.

Amide $C_6H_4Cl(SO_2NH_2)$: [148°]; plates.

Chloro-benzene *p*-sulphonic acid $C_6H_4Cl.SO_3H$ [1:4]. Formed by sulphonating chloro-benzene (Otto a. Brummer, *A.* 143, 102; Lindow a. Otto, *Z.* [2] 4, 39; Glutz, *A.* 143, 184). Also by the same method as the two preceding acids (Goslich, *A.* 180, 106). Deliquescent needles or prisms. Potash-fusion gives resorcin (Oppenheim a. Vogt, *A. Suppl.* 6, 376). The Na salt fused with KCN gives terephthalonitrile $C_6H_4(CN)_2$.

Salts.—NaA'aq. KA'.—AgA'.—CaA'_2 1½aq.—BaA'_2 2aq.—PbA'_2 2aq.—CuA'_2 5aq.

Chloride $C_6H_4Cl.SO_2Cl$. [53°].

Bromide $C_6H_4Cl.SO_2Br$. [53°].

Amide $C_6H_4Cl.SO_2NH_2$. [144°].

Anilide $C_6H_4Cl.SO_2NPhH$. [104°]. Needles (Wallach a. Huth, *B.* 9, 426).

Di-chloro-benzene sulphonic acid $C_6H_3Cl_2(SO_3H)$ [1:2:*x*]. From *o*-di-chloro-benzene and fuming H_2SO_4 at 210° (Beilstein a. Kurbatoff, *A.* 176, 41; 182, 94).—CaA'_2 2aq.—BaA'_2 2aq.—PbA'_2 2aq.

Di-chloro-benzene sulphonic acid $C_6H_3Cl_2(SO_3H)$ [1:3:*x*]. From *m*-di-chloro-benzene and fuming H_2SO_4 at 235° (B. a. K.).—CaA'_2 2aq.—BaA'_2 aq.—PbA'_2 3aq.

Di-chloro-benzene sulphonic acid $C_6H_3Cl_2(SO_3H)$ [1:4:*x*]. From *p*-di-chloro-benzene and vapours of SO_3 (Lesimple, *Z.* [2] 4, 226). Conc. H_2SO_4 has no action even at 210° (B. a. K.). Trimetric prisms (from water).—NH_4A'aq: needles, m. sol. water.—KA'aq. AgA'.—NaA'aq: six-sided tablets.—MgA'_2 6aq.—BaA'_2: laminæ.—PbA'_2 3aq.

Tri-chloro-benzene sulphonic acid $C_6H_2Cl_3(SO_3H)$ [1:3:4:6?]. From *u*-tri-chloro-benzene and fuming H_2SO_4 (Beilstein a. Kurbatoff, *A.* 192, 231).—CaA'_2 2aq.—BaA'_2 2aq.—PbA'_2 2aq.

CHLORO-BENZENE THIO-SULPHONIC ACID. *Chloro-phenyl ether* $C_{12}H_8Cl_2S_2O_2$ *i.e.* $C_6H_4Cl.SO_2.S.C_6H_4Cl$. [138°]. From chloro-benzene sulphinic acid and water at 130° (Otto, *A.* 145, 323). Small, four-sided, trimetric columns (from alcohol). Reduced by zinc and H_2SO_4 to chloro-phenyl mercaptan.

DI-CHLORO-BENZIDINE *v.* DI-CHLORO-DI-AMIDO-DIPHENYL.

CHLORO-BENZIL or Benzil chloride *v.* BENZILIC ACID, *Reaction* 5.

CHLORO-BENZO-TRICHLORIDE *v.* TETRA-CHLORO-TOLUENE.

***o*-CHLORO-BENZOIC ACID** $C_7H_5ClO_2$ *i.e.* $C_6H_4Cl(CO_2H)$ [1:2]. Mol. w. 156½. [137°]. S. ·114 at 0°. *Electrical conductivity*: Ostwald (*J. pr.* [2] 32, 349).

Formation.—1. From salicylic acid (1 mol.) and PCl_5 (2 mols.); the mixture is distilled and the portion (above 258°) containing $C_6H_4Cl.COCl$ is decomposed by water (Chiozza, *A. Ch.* [3] 36, 102; Kolbe a. Lautemann, *A.* 115, 184; Beilstein a. Reichenbach, *A.* 132, 311; Hubner, *Z.* 1870, 293; *A.* 147, 263; Wilkins a. Rack, *A.* 222, 192). 2. By boiling *o*-chloro-toluene with dilute $KMnO_4$ (Emmerling, *B.* 3, 880).—3. By heating *m*-chloro-nitro-benzene with alcoholic KCy at 260° (Richter, *B.* 4, 463).

Properties.—Large needles. Melts under water. V. sol. hot water, alcohol, and ether. Gives a yellow pp. in neutral solutions with Fe_2Cl_6.

Reactions.—1. *Soda-fusion* gives about equal quantities of *o*- and *m*-oxy-benzoic acids (Ost, *J. pr.* [2] 11, 385).—2. In hot aqueous solution it is reduced to benzoic acid by *sodium-amalgam*. Benzoic acid so prepared was called 'salylic' acid until Beilstein a. Schlun (*A.* 133, 239) showed it to be ordinary benzoic acid contaminated with a non-volatile substance which interfered with its crystallisation.—3. Fusion with *sodium formate* gives benzoic acid (V. Meyer, *B.* 3, 363; 4, 259).

Salts.—BaA'_2 3aq.—BaA'_2. S. 31 at 18·5°.—

CaA'_2 2aq: v. sol. water; v. sl. sol. alcohol.—AgA': scales (from boiling water).

Ethyl ether EtA'. (c. 240°) (Kekulé, *Rép. chim. pure*, 1861, 308).

Chloride $C_6H_4Cl.COCl$. (c. 237°).

Amide $C_6H_4Cl.CONH_2$: [139°]; needles; v. sl. sol. cold water; v. sol. alcohol and ether.

Anilide $C_6H_4Cl.CONPhH$: [114°]; needles.

p-Nitro-anilide $C_6H_4Cl.CO.NH.C_6H_4NO_2$: [180°]; from the anilide and HNO_3 (Wilkins a. Rack, *A.* 222, 192).

p-Toluide $C_6H_4Cl.CO.NHC_6H_4(CH_3)$: [131°]; colourless crystals; sol. alcohol, nearly insol. water (Schreib, *B.* 13, 465).

m-Nitro-p-toluide $C_6H_4Cl.CO.NHC_6H_3(CH_3)(NO_2)$: [139°]; yellowish crystals; sol. acetic acid, sl. sol. alcohol, insol. water. Prepared by nitration of the *p*-toluide.

Di-nitro-p-toluide $C_6H_4Cl.CO.NHC_6H_2(CH_3)(NO_2)_2$(?): [228°]; colourless crystals. Sl. sol. alcohol, v. sol. acetic acid and chloroform. Prepared by further nitration of the mono-nitro- compound.

Tri-nitro-p-toluide $C_{14}H_9N_4O_7Cl$: [239°]; colourless crystals. Prepared by still further nitration of the above.

m-Amido-p-toluide $C_6H_4Cl.CO.NHC_6H_3(CH_3)(NH_2)$: [153°]; colourless crystals; sol. alcohol. Prepared by reduction of the *m*-nitro-*p*-toluide.—B'HCl.—$B'HNO_3$.

Benzoylamido-p-toluide $C_6H_4Cl.CO.NHC_6H_3(CH_3)(NHBz)$: [178°]; colourless needles, sl. sol. alcohol.

Nitrile $C_6H_4Cl.CN$. *o-Chloro-cyano-benzene.* [43°]. (232°). From the amide and PCl_5 or P_2S_5. Also from the amide or nitrile of salicylic acid by the action of PCl_5 (Henry, *B.* 2, 492). Long needles: sl. sol. boiling water: m. sol. alcohol and ether.

***m*-Chloro-benzoic acid** $C_6H_4Cl.CO_2H$ [1:3]. [153°]. S. ·035 at 0°. *Electrical conductivity*: Ostwald, *J. pr.* [2] 32, 349.

Formation.—1. By chlorinating benzoic acid by treatment with chlorine, with HCl and $KClO_3$, or with a boiling solution of bleaching powder (Herzog, *N. Br. Arch.* 23, 15; Scharling, *A.* 41, 49; 42, 268; Stenhouse, *A.* 55, 1; Field, *A.* 65, 55; Otto, *A.* 122, 157; Hübner a. Weiss, *B.* 6, 175).—2. From *m*-amido-benzoic acid by the diazo- reaction.—3. By distilling *m*-sulpho-benzoic acid (1 mol.) with PCl_5 (2 mols.) and treating the resulting *m*-chloro-benzoyl chloride with water (Limpricht a. Uslar, *A.* 102, 259).—4. By oxidation of *m*-chloro-toluene with chromic acid mixture (Wroblewsky, *A.* 168, 200).—5. From *p*-chloro-nitro-benzene and KCy at 200° (Richter, *B.* 4, 463).—6. From *s*-chloro-amido-benzoic acid by removing NH_2 by the diazo- reaction (Hubner, *A.* 222, 91).

Properties.—Long needles or small prisms. Does not melt under water.

Reactions.—1. *Sodium amalgam* reduces it to benzoic acid (Beilstein a. Reichenbach, *A.* 132, 315).—2. *Potash-fusion* gives *m*-oxy-benzoic acid (Dembey, *A.* 148, 222).

Salts.—CaA'_2 3aq: small needles. S. 1·21 at 12°.—BaA'_2 4aq: small needles.—AgA'.

Ethyl ether $C_6H_4Cl.CO_2Et$: (245°); liquid.

Chloride $C_6H_4Cl.COCl$: (225°); liquid.

Amide $C_6H_4Cl.CONH_2$: [133°]; needles.

Nitrile $C_6H_4Cl.CN$: [39°]. Formed by distilling *m*-sulpho-benzamide with PCl_5 (Limpricht a. Uslar, *A.* 106, 35). Also from the nitrile of *m*-amido-benzoic acid by displacement of NH_2 by Cl (Griess, *B.* 2, 370). Needles; insol. water. Volatile with steam.

***p*-Chloro-benzoic acid** $C_6H_4Cl.CO_2H$ [1:4]. *Chloro-dracylic acid.* [236°]. S. ·019. *Electrical conductivity*: Ostwald, *J. pr.* [2] 32, 349.

Formation.—1. From *p*-amido-benzoic acid by diazo- reaction (Wilbrand a. Beilstein, *A.* 128, 257; Beilstein a. Schlun, *A.* 133, 242).—2. By oxidation of *p*-chloro-toluene with CrO_3 (Beilstein a. Geitner, *A.* 139, 336) or dilute $KMnO_4$ (Emmerling, *B.* 8, 880).—3. From chloro-benzene, dilute H_2SO_4, and MnO_2 (Carl Muller, *Z.* [2] 5, 137).

Properties.—Needles (by sublimation); v. sl. sol. water, v. sol. alcohol and ether. *Sodium amalgam* reduces it to benzoic acid (Hartmann, *J. pr.* [2] 12, 204).

Salts.—BaA'_2 4aq.—CaA'_2 3aq.—AgA'.

Methyl ether MeA': [42°]; needles.

Chloride $C_6H_4Cl.COCl$. [222°].

Amide $C_6H_4Cl.CONH_2$: [170°]; needles.

Anilide $C_6H_4Cl.CONPhH$: [194°]; needles.

Di-chloro-benzoic acid $C_6H_3Cl_2(CO_2H)$ [6:2:1]. Mol. w. 191. [126·5°]. Formed, together with the two isomerides [156°] and [201°], by the action of water on crude penta-chloro-toluene $C_6H_3Cl_2.CCl_3$ at 200° (Schultz, *A.* 187, 269). Slender needles; volatile with steam.

Salts.—KA' 5aq.—NH_4A' aq.—BaA'_2 3½aq. S. (of BaA'_2 in alcohol) 3·8 at 4°.—ZnA'_2 1½aq.

Chloride $C_6H_3Cl_2.COCl$: (244°); liquid.

Amide $C_6H_3Cl_2.CONH_2$: [166°]; needles.

Di-chloro-benzoic acid $C_6H_3Cl_2CO_2H$ [2:5:1]. [156°]. (301°). S. ·0850 at 14°.

Formation.—1. From chloro-nitro-benzoic acid [164°] by reduction and displacement of NH_2 by Cl by means of the diazo- reaction (Wilkens a. Rack, *A.* 222, 201).—2. From crude penta-chloro-toluene $C_6H_3Cl_2.CCl_3$, together with the acids [126·5°] and [201°] (Schultz, *A.* 187, 268).—3. By chlorinating *o*-chloro-benzoic acid in presence of $SbCl_5$ (Beilstein, *A.* 179, 286). Occurs also among products of chlorination of benzoic acid.—4. By oxidising (6, 3, 1)-di-chloro-ethyl-benzene with chromic mixture (Istrati, *A. Ch.* [6] 6, 479).—5. From $C_6H_3MeCl_2$ [1:2:5] and dilute HNO_3 (Lellmann a. Klotz, *A.* 231, 319).

Needles (from water); slightly volatile with steam. Heated with dilute H_2SO_4 at 220° it gives CO_2 and *p*-dichloro-benzene.—BaA'_2 3aq. S. (of BaA'_2) 2·5 at 14·4°.—CaA'_2 2aq.—PbA'_2 aq.—CuA'_2 2aq (B.).—CuA'_2 aq (I.).—FeA'_2.—KA' 2aq. NH_4A': slender needles.—AgA'.

Ethyl ether EtA'. (271° i. V.). S.G. ♀ 1·328.

Amide $C_6H_3Cl_2.CONH_2$: [155°]; needles (B.).

Anilide: [240°]; prisms (from benzene).

Di-chloro-benzoic acid $C_6H_3Cl_2(CO_2H)$ [3:2:1]. [156°] (C.); [166°] (S.). Formed, together with the isomeride [201°], by chlorination of benzoic acid (Claus, *B.* 5, 658; 6, 721; 8, 948; 20, 1621). Formed also by oxidising *c*-di-chloro-toluene with $KMnO_4$ (Seelig, *A.* 237, 162). Not affected by dilute H_2SO_4 at 220°. Distillation over lime gives *o*-di-chloro-benzene. Not decomposed by conc. H_2SO_4 at 300°.—BaA'_2 3aq. S. 8 at 28°.

Di-chloro-benzoic acid $C_6H_3Cl_2(CO_2H)$ [4:2:1]. [158°]. From $C_6H_3MeCl_2$ [1:2:4] and dilute HNO_3 (Lellmann a. Klotz, *A.* 231, 315).

Salt.—BaA'_2 3½aq.

Di-chloro-benzoic acid $C_6H_3Cl_2(CO_2H)$ [3:5:1]. [182°]. From $C_6H_3MeCl_2$ and dilute HNO_3 (Lellmann a. Klotz, *A.* 231, 324). Needles (from dilute alcohol). May be sublimed.

Di-chloro-benzoic acid $C_6H_3(CO_2H)Cl_2$ [4:3:1]. [201°].

Formation.—1. A product of the chlorination of benzoic acid (Beilstein a. Kuhlberg, *A.* 152, 232; 179, 291).—2. From chloro-sulpho-benzoic acid and PCl_5 (Otto, *A.* 123, 226). 3. By oxidation of $C_6H_4Cl_2.CH_3$ or $C_6H_3Cl_2.CH_2Cl$; or by heating $C_6H_3Cl_2.CCl_3$ with water at 200° (B. a. K.). 4. From *p*-chloro-benzoic acid and $SbCl_5$ at 200° (B.).—5. From chlorinated *p*-oxy-benzoic acid and PCl_5 (Lössner, *J. pr.* [2] 13, 433).—6. From $C_6H_3MeCl_2$ [1:3:4] by dilute HNO_3 (Lellmann a. Klotz, *A.* 231, 313).

Properties.—Very slender needles (from water); volatile with steam.

Salts—CaA'_2 3aq.—BaA'_2 4aq. S. 1·1 at 18°.

Ethyl ether EtA′: (263°); liquid.

Chloride $C_6H_3Cl_2.COCl$: (242°); liquid.

Amide $C_6H_3Cl_2.CONH_2$: [133°]; needles.

Tri-chloro-benzoic acid $C_6H_2Cl_3(CO_2H)$ [6:3:2:1]. [c. 80°]. From the corresponding aldehyde and $KMnO_4$ (Seelig, *A.* 237, 150). Needles, v. sol. water.

Tri-chloro-benzoic acid $C_6H_2Cl_3(CO_2H)$ [4:3:2:1]. Mol. w. 225½. [129°]. From the corresponding (4, 3, 2, 1)-tri-chloro-benzoic aldehyde by $KMnO_4$ (Seelig, *A.* 237, 150). Needles; m. sol. water.

Tri-chloro-benzoic acid $C_6H_2Cl_3(CO_2H)$ [5:4:2:1]. [163°]. From *s*-tri-chloro-toluene by oxidation with chromic acid mixture (Jannasch, *A.* 142, 301). Formed also by boiling benzoic acid with water and bleaching-powder for a long time; and by heating $C_6H_2Cl_3.CCl_3$ with water at 260° (Beilstein a. Kuhlberg, *A.* 152, 234). Slender needles (from water or by sublimation); v. sl. sol. cold water.

Salts.—NH_4A'.—CaA'_2 2aq.—BaA'_2 7aq.—SrA'_2 4aq

Ethyl ether EtA′: [65°]; needles.

Chloride $C_6H_2Cl_3.COCl$. [41°]. (272°).

Amide $C_6H_2Cl_3.CONH_2$: [168°]; needles.

Tri-chloro-benzoic acid $C_6H_2Cl_3(CO_2H)$ [5:4:3:1]. [203°].

Formation.—1. From di-nitro-*p*-amido-benzoic acid and fuming HCl at 210° (Salkowski, *A.* 163, 28).—2. From crude hexa-chloro-toluene $C_6H_2Cl_3.CCl_3$ and NaOH (Claus a. Bücher, *B.* 20, 1626).

Properties.—Slender needles (from dilute alcohol or by sublimation).

Salts.—AgA′.—BaA'_2 4aq.—CaA'_2 6aq.

Ethyl ether EtA′: [86°]; slender needles (S.).

Chloride $C_6H_2Cl_3.COCl$. [36°] (S.).

Amide $C_6H_2Cl_3.CONH_2$. [176°] (S.).

c-**Tetra-chloro-benzoic acid** $C_6HCl_4(CO_2H)$. [165°]. Formed by chlorination of the di-chloro-benzoic acids melting at [201°] and [156°] (Claus) by heating with MnO_2 and fuming HCl at 190° (Claus a. Bucher, *B.* 20, 1626). Also from di-chloro-benzoic acid [156°] and $SbCl_5$ at 230° (Beilstein, *A.* 179, 286).—BaA'_2 4aq (B.).—BaA'_2 3½aq (C.).

Tetra-chloro-benzoic acid $C_6HCl_4(CO_2H)$ [5:4:3:2:1]. [186°]. Prepared by heating tetra-chloro-phthalic acid with acetic acid (2 or 3 pts.) at 300° for 3 or 4 hours (Tust, *B.* 20, 2439; 21, 1532.) Long colourless needles. V. sol. alcohol and ether, v. sl. sol. water.

Salts.—A'_2Ca 4aq: long colourless needles; m. sol. hot water.—A'_2Cu 3½aq.—BaA'_2 3½aq.

Ethyl ether A′Et: [35°]; long colourless needles.

Tetra-chloro-benzoic acid $C_6HCl_4(CO_2H)$ [6:4:3:2:1]? [186°]. From hepta-chloro-toluene $CHCl_4.CCl_3$ and water at 280° (Beilstein a. Kuhlberg, *A.* 152, 245).

Penta-chloro-benzoic acid $C_6Cl_5(CO_2H)$. [200°]. Formed by chlorination of the di-chloro-benzoic acids [201°] and [156°] with MnO_2 and HClAq at 190° (C. a. B.).—BaA'_2 4aq: stellate groups of needles.

Nitrile $C_6Cl_5(CN)$. [210°]. Formed by exhaustive chlorination of benzonitrile with $SbCl_5$ (Merz a. Weith, *B.* 16, 2885). Colourless needles. Sublimable. V. sol. hot alcohol, chloroform, and CS_2, sl. sol. cold alcohol and ether. It is very stable towards HCl at high temperatures. Alcoholic NaOH removes all its chlorine at 200°.

o-**CHLORO-BENZOIC ALDEHYDE** [2:1] $C_6H_4Cl.CHO$. (c. 215°). S.G. ^{8} 1·29. Formed by heating tri-chloro-toluene $C_6H_4Cl.CHCl_2$ (from salicylic aldehyde and PCl_5) with water at 170° or with ($\frac{9}{16}$ pt.) dry oxalic acid at 130° (Henry, *B.* 2, 135; Anschutz, *A.* 226, 19). Oil, smelling of almonds; volatile with steam. Forms a crystalline compound with $NaHSO_3$.

p-**Chloro-benzoic aldehyde** [4:1] $C_6H_4Cl.CHO$. [48°]. (c. 212°). Obtained by boiling $C_6H_4Cl.CHBr_2$ [48°] (10 pts.) with lead nitrate (4 pts.) and water (100 pts.) for three days, in presence of CO_2 (Jackson a. White, *Am.* 3, 31; *N. Am. A.* 15, 268; *B.* 11, 1042). Formed by boiling $C_6H_4Cl.CH_2Cl$ with aqueous lead nitrate. Formed also by passing chlorine into benzoic aldehyde containing iodine (Beilstein a. Kuhlberg, *A.* 147, 339). Long needles; may be sublimed. Sol. alcohol, ether, CS_2, and HOAc, sl. sol. water. Absorbs oxygen from the air. Forms a crystalline compound with $NaHSO_3$.

Di-chloro-benzoic aldehyde $C_6H_3Cl_2.CHO$ [5:2:1]. [58°]. (230°–233°). Preparation not given. White crystals. On oxidation it gives di-chloro-benzoic acid [152°] (Gnehm, *B.* 17, 752).

Di-chloro-benzoic aldehyde $C_6H_3Cl_2.CHO$ [6:2:1]. [illegible]. Formed by heating $C_6H_3Cl_2.CHCl_2$ with water at 200° (Beilstein a. Kuhlberg, *A.* 152, 224). Slender needles; volatile with steam; sl. sol. hot water. Attacks the eyes. Combines with $NaHSO_3$. Oxidises to di-chloro-benzoic acid [128°].

(β)-**Di-chloro-benzoic aldehyde** $C_6H_3Cl_2.CHO$ [4:2:1]. [71°]. (c. 233°). Formed by the action of conc. H_2SO_4 on $C_6H_3Cl_2.CHCl_2$. The aldehyde is separated by means of the double compound with sodium bisulphite (Seelig, *A.* 237, 167). White needles (from alcohol). Oxidation with permanganate yields (β)-dichloro-benzoic acid [158°]. When heated with Ac_2O and NaOAc it forms (β)-di-chloro-cinnamic acid [228°].

Tri-chloro-benzoic aldehyde $C_6H_2Cl_3.CHO$ [113°]. Formed by heating $C_6H_2Cl_3.CHCl_2$ (281°) with water at 250° (B. a. K.; Seelig, *B.* 18, 420; *A.* 237, 148). Very slender needles;

**Insol. boiling water, v. sol. alcohol; volatile with steam. Conc. H_2SO_4 and KNO_3 form tri-chloro-nitro-benzoic acid [222°] and an aldehyde [124°].

Tri-chloro-benzoic aldehyde $C_6H_2Cl_3.CHO$ [4:3:2:1]. [90°]. From penta-chloro-toluene $C_6H_2Cl_3.CHCl_2$ [84°] (Seelig). Gives on oxidation tri-chloro-benzoic acid [129°].

CHLORO-BENZONITRILE *v.* Nitrile of Chloro-benzoic acid.

CHLORO-BENZOPHENONE $C_6H_4Cl.CO.C_6H_5$. *Phenyl chloro-phenyl ketone.* [76°]. (above 300°). From chloro-benzene, benzoic acid, and P_2O_5 (Kollarits a. Merz, *B.* 6, 517). Flat needles (from ether-alcohol); v. sol. ether, sl. sol. cold alcohol and ligroïn.

CHLORO-*o*-BENZOYL-BENZOIC ACID $C_{14}H_9ClO_3$ *i.e.* $C_6H_5.CO.C_6H_3Cl(CO_2H)$ [2:4or5:1]. *Chloro-benzophenone carboxylic acid.* [171°]. From chloro-phthalic anhydride [97°], benzene, and Al_2Cl_6 (Græbe a. Rée, *C. J.* 49, 531; *A.* 233, 239). Minute monoclinic prisms; v. sol. ether and alcohol, sl. sol. CS_2, v. sl. sol. light petroleum. Conc. H_2SO_4 converts it into chloro-anthraquinone [204°].

Di-chloro-*o*-benzoyl-benzoic acid $C_6H_5.CO.C_6H_2Cl_2.CO_2H$. [159°]. From (β)-di-chloro-phthalic anhydride [150°], benzene, and Al_2Cl_6 (Le Royer, *A.* 238, 356). Needles (from dilute alcohol).

Tetra-chloro-*o*-benzoyl-benzoic acid $C_{14}H_6Cl_4O_3$ *i.e.* $C_6H_5.CO.C_6Cl_4.CO_2H$. [200°]. From tetra-chloro-phthalic anhydride, benzene, and Al_2Cl_6 (Kircher, *A.* 238, 338). White needles; sl. sol. cold benzene, v. e. sol. alcohol, insol. water. Cannot be distilled or sublimed.

Reactions.—1. *Soda-fusion* gives benzoic acid. 2. H_2SO_4 and PCl_5 give tetra-chloro-anthraquinone.—3. HI gives tetra-chloro-benzyl-benzoic acid.

Salts.—NaA′ 4aq. S. 1·7 at 20°.—KA′ $1\frac{1}{2}$aq. —CuA'_2 2aq.—CuA'_2CuO.

Ethers: EtA′ [90°].—MeA′ [92°].

Chloride [183°]. Needles.

CHLORO-BENZOYL CHLORIDE *v.* *Chloride* of Chloro-benzoic acid.

CHLORO-DIBENZYL *v.* Chloro-di-phenyl-ethane.

***p*-CHLORO-BENZYL ACETATE** $C_9H_9ClO_2$ *i.e.* [4:1] $C_6H_4Cl.CH_2.OAc$. (240°). From $C_6H_4Cl.CH_2Cl$ and KOAc in boiling alcohol (Beilstein a. Kuhlberg, *A.* 147, 344).

Di-chloro-benzyl acetate $C_6H_3Cl_2.CH_2OAc$. (259°). Similarly prepared from $C_6H_3Cl_2.CH_2Cl$ (B. a. K.).

CHLORO-BENZYL-ACETO-ACETIC ETHER $C_{13}H_{15}ClO_3$ *i.e.* $CH_3.CO.CH(CHClPh).CO_2Et$(?) [41°]. Formed, together with an isomeride [72°] possibly $CH_3.CO.CCl(CH_2Ph).CO_2Et$, by mixing aceto-acetic ether with benzoic aldehyde and saturating with HCl (*v.* vol. i. p. 24).

***p*-CHLORO-BENZYL ALCOHOL** C_7H_7ClO *i.e.* $C_6H_4Cl.CH_2OH$. [66°] (B. a. K.); [71°] (J. a. F.). Obtained by heating *p*-chloro-benzyl acetate (*v. supra*) with alcoholic NH_3 at 160° (Beilstein a. Kuhlberg, *A.* 147, 344; Neuhof, *Z.* [2] 3, 467). Prepared by boiling *p*-chloro-benzyl chloride $C_6H_4Cl.CH_2Cl$ with water (Jackson a. Field, *Am.* 2, 88; *P. Am. A.* 14, 56). Needles (by sublimation or from water): may be distilled. Sol. hot water, alcohol, and ether. Chromic mixture oxidises it to *p*-chloro-benzoic acid [233°].

Di-chloro-benzyl alcohol $C_6H_3Cl_2.CH_2OH$. [77°]. From the acetate (*v. supra*) by heating with alcoholic ammonia at 180° (B. a. K.). Needles; v. sl. sol. water.

Tri-chloro-benzyl alcohol $C_6H_2Cl_3.CH_2OH$. From tri-chloro-benzyl chloride $C_6H_2Cl_3.CH_2Cl$ and alcoholic KOAc at 150°. Crystalline (Beilstein a. Kuhlberg, *A.* 152, 241).

Tetra-chloro-benzyl alcohol $C_6HCl_4.CH_2OH$. From $C_6HCl_4.CH_2Cl$, alcohol, and KOAc at 180°; crystallised from water (B. a. K.).

Penta-chloro-benzyl alcohol $C_6Cl_5.CH_2OH$. [193°]. From $C_6Cl_5.CH_2Cl$, alcohol, and KOAc at 200° (B. a. K.). White needles (from benzene-alcohol); insol. water, sl. sol. boiling alcohol.

***p*-CHLORO-BENZYLAMINE** C_7H_8ClN *i.e.* [4:1] $C_6H_4Cl.CH_2NH_2$. *p*-Chloro-benzyl chloride (1 vol.) heated with alcoholic ammonia (2 vols.) at 100° forms $(C_6H_4Cl.CH_2)NH_2$, $(C_6H_4Cl.CH_2)_2NH$ and $(C_6H_4Cl.CH_2)_3N$. Their hydrochlorides may be separated by crystallisation from alcohol (Berlin, *A.* 151, 137; Jackson a. Field, *Am.* 2, 94; *P. Am. A.* 14, 56). Colourless oil; sol. ether.

Salts. —×B′HCl: [241°]; narrow plates, sol. water and alcohol. —$B'_2H_2PtCl_6$: yellow needles. ×B′HBr: [230°]; decomposed by melting.—×$B'_2H_2CO_3$: [115°]; plates (from water) or needles (from alcohol).

Di-*p*-chloro-di-benzyl-amine $(C_6H_4Cl.CH_2)_2NH$. [29°]. From chloro-benzyl bromide and alcoholic NH_3 (Jackson a. Field, *Am.* 2, 90; *B.* 11, 904). White blades; insol. water, sol. alcohol, ether, benzene, and CS_2.

Salts.—B′HCl: [288°]; plates, sol. water and alcohol, insol. ether. —$B'_2H_2PtCl_6$: yellow scales, sl. sol. boiling water, insol. alcohol.—B′HBr: [280°–290°], melting with decomposition. Scales, sl. sol. water, insol. ether.

(β)-Di-chloro-di-benzyl-amine $(C_6H_4Cl.CH_2)_2NH$. This base occurs, together with the two following, among the products of the action of alcoholic NH_3 on crude chloro-benzyl chloride (Berlin, *A.* 151, 141).—B′HCl: [228°]. B′HBr: [224°].—B′HI: [215°].—$B'HNO_3$: [204°].

(γ)-Di-chloro-di-benzyl-amine $(C_6H_4Cl.CH_2)_2NH$. **Salts.**—B′HCl: [220°].—B′HBr: [212°].—B′HI: [187°].—$B'HNO_3$: [193°].

(δ)-Di-chloro-di-benzyl-amine $(C_6H_4Cl.CH_2)_2NH$. **Salts.**—B′HCl: [222°].—B′HBr: [199°].—B′HI: [218°].—$B'HNO_3$: [179°].

Tri-*p*-chloro-tri-benzyl-amine $(C_6H_4Cl.CH_2)_3N$. [79°]. From *p*-chloro-benzyl bromide and alcoholic NH_3 (J. a. F.). Needles; sol. hot alcohol, ether, benzene, and CS_2.

Salts.—B′HCl 2aq: [196°].—$B'_2H_2PtCl_6$: pale orange plates, insol. water, alcohol, and ether.

TETRA-CHLORO-*o*-BENZYL-BENZOIC ACID $C_6H_5.CH_2.C_6Cl_4.CO_2H$. *Tetra-chloro-di-phenyl-methane eso-carboxylic acid.* [157°]. From $C_6H_5.CO.C_6Cl_4.CO_2H$ and conc. HI at 180° (Kircher, *A.* 238, 343). Hair-like needles (from dilute alcohol). Insol. water, v. sol. alcohol.

Salts. NaA′ 1aq.—AgA′.

CHLORO-BENZYL BROMIDE *v.* Chloro-bromo-toluene.

CHLORO-BENZYL CHLORIDE *v.* Di-chloro-toluene.

CHLORO-BENZYL CYANIDE *v.* *Nitrile* of Chloro-phenyl-acetic acid.

***p*-CHLORO-BENZYL ETHYL OXIDE** $C_6H_4Cl.CH_2.O.C_2H_5$. (217°) (Sintenis, *A.* 161, 335); (215°–225°) (Jackson a. White, *Am.* **2**, 170); (226°) (Errera, *G.* 17, 206). From *p*-chloro-benzyl chloride (acetate or bromide) and alcoholic KOH (Naquet, *A. Suppl.* 2, 251). Liquid, with fruity odour; decomposed by heating above its boiling-point into *p*-chloro-benzoic aldehyde and ethane (E.).

ω-CHLORO-BENZYLIDENE-ANILINE $C_6H_5.N:CCl.C_6H_5$ *Benzanilide-imide-chloride.* [41°]. Formed by isomeric change of the first formed oxim-chloride $(C_6H_5)_2C:NCl$ by the action of PCl_5 or $POCl_3$ upon benzophenone-oxim $(C_6H_5)_2C:NOH$. Colourless rhombic tables (Beckmann, *B.* 19, 989).

CHLORO-BENZYLIDENE CHLORIDE *v.* TRI-CHLORO-TOLUENE.

***o*-CHLORO-BENZYLIDENE-MALONIC ACID** $C_{10}H_7ClO_4$ *i.e.* $C_6H_4Cl.CH:CH(CO_2H)_2$. [192°]. Formed by heating malonic acid with *o*-chloro-benzoic aldehyde and HOAc for some hours at 100° (Stuart, *C. J.* 53, 141). Decomposed on melting into CO_2 and chloro-cinnamic acid. Boiling water splits it up into *o*-chloro-benzoic aldehyde and malonic acid.

ω-CHLORO-BENZYLIDENE-(α)-NAPHTHYL-AMINE $C_6H_5CCl:N.C_{10}H_7$. [60°]. From benzoyl-(α)-naphthylamine and PCl_5 (Just, *B.* 19, 979).

ω-Chloro-benzylidene-(β)-naphthylamine. [68°]. Similarly prepared (J.). Leaflets; slowly converted into benzoyl-(β)-naphthylamine on exposure to the air.

CHLORO-BENZYLIDENE-PHTHALIMIDINE $C_{15}H_{10}ClNO$. [232°]. From benzylidene-phthalimidine and PCl_5 (Gabriel, *B.* 18, 1260). Needles (from alcohol).

ω-CHLORO-BENZYLIDENE-*o*-TOLUIDINE $C_{14}H_{12}ClN$ *i.e.* $C_6H_4Me.N:CCl.C_6H_5$ *Benzoyl-o-toluidine-imide-chloride.* Formed by the action of PCl_5 upon benzoyl-*o*-toluidine. Water regenerates benzoyl-*p*-toluidine. The compound was not obtained in a pure state. With sodio-malonic ether it gives *o*-tolyl-β-imido-benzyl-malonic ether $C_6H_5.C(NC_7H_7).CH(CO_2Et)_2$ (Just, *B.* 19, 982).

ω-Chloro-benzylidene-*m*-toluidine $C_{14}H_{12}ClN$ *i.e.* $C_6H_4Me.N:CCl.C_6H_5$. Formed by the action of PCl_5 upon benzoyl-*m*-toluidine. Not obtained in a pure state. By the action of sodio-malonic ether it yields *m*-tolyl-β-imido-benzyl-malonic ether $C_6H_5.C(NC_7H_7).CH(CO_2Et)_2$ (Just, *B.* 19, 983).

ω-Chloro-benzylidene-*p*-toluidine $C_6H_4Me.N:CCl.C_6H_5$. [52°]. Formed by gently warming benzoyl-*p*-toluidine with PCl_5. Large clear prismatic crystals. By boiling with water or alcohol it is reconverted into the benzoyl-*p*-toluidine. With *p*-toluidine it yields di-*p*-tolyl-benzamidine $C_6H_5.C(NC_7H_7)NHC_7H_7$. With sodio-malonic ether it gives *p*-tolyl-β-imido-benzyl-malonic ether $C_6H_5.C(NC_6H_4Me).CH(CO_2Et)_2$ (Just, *B.* 19, 979).

CHLORO-BENZYL-MALONIC ETHER $C_6H_5.CH_2.CCl(CO_2Et)_2$. (305°). S.G. $\frac{19}{15}$ 1·150. Prepared by the action of benzyl chloride (26 pts.) on chloro-malonic ether (38·8 pts.) and NaOEt (from 4·6 pts. Na and 70 pts. alcohol) (Conrad, *A.* 209, 243; *B.* 13, 2159). Liquid. Decomposed by KOH into alcohol, benzyl-tartronic acid $C_6H_5.CH_2.C(OH)(CO_2H)_2$, and a little cinnamic acid.

Amide $C_8H_7Cl(CO.NH_2)_2$. (c. 80°). White needles. Sol. alcohol, insol. water. (Bischoff a. Emmert, *B.* 15, 1112).

***p*-CHLORO-BENZYL MERCAPTAN** C_7H_7ClS *i.e.* [4:1] $C_6H_4Cl.CH_2.SH$. [20°] (J. a. W.). From *p*-chloro-benzyl bromide (or chloride) and alcoholic KHS (Beilstein, *A.* 116, 347; 147, 346; Jackson a. White, *Am.* 2, 167; *P. Am. A.* 14, 312). Nauseous liquid or white crystals. Mixes with alcohol, ether, benzene, and CS_2.—$(C_7H_6ClS)_2Hg$: from the mercaptan and ppd. HgO; needles; insol. water, sl. sol. ether and alcohol.

DI-*p*-CHLORO-DI-BENZYL SULPHIDE $C_{14}H_{12}Cl_2S$ *i.e.* $(C_6H_4Cl.CH_2)_2S$. [42°]. From *p*-chloro-benzyl bromide and alcoholic Na_2S (Jackson a. White, *P. Am. A.* 14, 312; *Am.* 2, 166; *B.* 13, 1217). Thick needles, insol. water, v. sol. alcohol, ether, benzene and CS_2.

Di-*p*-chloro-di-benzyl disulphide $C_{14}H_{12}Cl_2S_2$ *i.e.* $(C_6H_4Cl.CH_2)_2S_2$. [59°]. From *p*-chloro-benzyl bromide and alcoholic Na_2S_2 (J. a. W.). Flat needles, with disagreeable smell. V. sol. alcohol, HOAc, ligroin, ether, benzene, and CS_2.

***p*-CHLORO-BENZYL SULPHOCYANIDE** $C_6H_4Cl.CH_2S.CN$. [17°]. Prepared by boiling an alcoholic solution of *p*-chloro-benzyl bromide with KCNS (Jackson a. Field, *Am.* 2, 91). White flat needles.

DI-*p*-CHLORO-DI-BENZYL-SULPHONE $C_{14}H_{12}Cl_2SO_2$ *i.e.* $(C_6H_4Cl.CH_2)_2SO_2$. [165°]. Formed, together with $C_6H_4Cl.CH_2SO_3H$, by the action of K_2SO_3 on *p*-chloro-benzyl chloride (Henninger a. Vogt, *A.* 166, 374). Prepared by oxidising *p*-chloro-benzyl sulphide with CrO_3 (Jackson a. White, *Am.* 2, 167; *P. Am. A.* 14, 312). Very small needles (from alcohol); insol. water, sol. alcohol, ether, HOAc, and CS_2.

Isomerides [149°] and [185°] are formed when crude chloro-benzyl chloride is used (H. a. V.).

CHLORO-BENZYL SULPHONIC ACID *v.* CHLORO-TOLUENE SULPHONIC ACID.

DI-*p*-CHLORO-DI-BENZYL DI-SULPHOXIDE $(C_6H_4Cl.CH_2)_2S_2O_2$. [120°]. Obtained by oxidising di-*p*-chloro-di-benzyl disulphide with CrO_3 in HOAc (Jackson a. White, *Am.* 2, 169; *P. Am. A.* 14, 315). Waxy solid, becoming crystalline; insol. water, v. sol. alcohol and ether.

DI-CHLORO-BETORCIN $C_6Cl_2Me_2(OH)_2$. [142°]. Prepared by adding tetra-chloro-betorcin in small portions to boiling hydric iodide (15 p.c.). Crystallised from light petroleum (50 pts.) (Stenhouse a. Groves, *C. J.* 37, 395). Colourless needles. Sol. CS_2, benzene and ether.

Tetra-chloro-betorcin $C_6Cl_2Me_2(OCl)_2$. [109°]. Prepared by adding a solution of betorcin to a slight excess of chlorine hydrate (ice and water saturated with Cl). The crystals which separate after 12 hours are recrystallised from light petroleum. The yield is quantitative (Stenhouse a. Groves, *C. J.* 37, 399).

Properties.—Large white prisms. V. sol. benzene and ether, insol. water.

CHLORO-BROMAL *v.* CHLORO-DI-BROMO-ACETIC ALDEHYDE.

CHLORO-BROMALIDE $C_5H_2Cl_4Br_2O_3$. [122°]. Colourless prisms. Formed by heating di-chloro-

bromo-acetic aldehyde with H_2SO_4 (Jacobsen a. Neumeister, *B.* 15, 600).

CHLORO-BROMANILIC ACID *v.* CHLORO-BROMO-DI-OXY-QUINONE.

CHLORO-BROMO-ACETIC ACID $CHClBr.CO_2H$. [201°]. Prepared by heating chloro-acetic acid (1 mol.) with bromine (1 mol.) at 160° (Cech a. Steiner, *B.* 8, 1174). Pungent liquid; attacks the skin. Its salts are v. sol. water.

Ethyl ether EtA'. (c. 162°). Smells like peppermint; partially decomposed on boiling.

Amide $CHClBr.CONH_2$: [126°]; needles.

Chloro-di-bromo-acetic acid $CClBr_2.CO_2H$. [89°]. (233°). Formed by oxidation of the corresponding aldehyde with HNO_3 (Neumeister, *B.* 15, 603). Trimetric plates (from conc. HNO_3). By alkalis it is split up into CO_2 and chloro-di-bromo-methane.

Salts.—KA' 2aq: glistening soluble prisms. —PbA'_2 aq, sparingly soluble slender needles.

Ethyl ether A'Et: (203°); liquid.

Amide $CClBr_2.CONH_2$: [127°]; small transparent dimetric tables; v. sol. ether and chloroform, sl. sol. benzene and CS_2. Formed together with $CHClBr_2$ by the action of dry NH_3 upon di-chloro-tetra-bromo-acetone $CClBr_2.CO.CClBr_2$ dissolved in ether (Levy a. Jedlička, *B.* 20, 2320).

Di-chloro-bromo-acetic acid $CCl_2Br.CO_2H$. [64°]. (215°). Formed by oxidation of the corresponding aldehyde with HNO_3 (Neumeister, *B.* 15, 602). Large prisms. V. sol. water and alcohol. By boiling with alkalis it is split up into di-chloro-bromo-methane and CO_2.

Salts.—KA' 3aq: long trimetric prisms.— NaA' 5aq: large tables, sol. water, alcohol, and ether. — $^{x}NH_4A'$: long fine needles. —PbA'_2 aq: sparingly soluble glistening prisms.

Ethyl ether A'Et: (189°); liquid.

Amide [139°]; (254°); tables. Sol. alcohol and ether; insol. chloroform.

CHLORO-DI-BROMO-ACETIC ALDEHYDE $CClBr_2.CHO$. *Chlorobromal.* (149°). S.G. ^{15} 2·2793. Prepared by the action of bromine on chloro-acetal $CH_2Cl.CH(OEt)_2$. Liquid. By treatment with KOH it gives chloro-di-bromo-methane (Jacobsen a. Neumeister, *B.* 15, 600).

Hydrate $CClBr_2.CH(OH)_2$. *Chloro-di-bromo-acetic orthaldehyde.* [52°]; small prisms.

Alcoholate $CClBr_2.CH(OH)(OEt)$: [46°]; long needles.

Combination with Acetamide [158°].

Di-chloro-bromo-acetic aldehyde $CCl_2Br.CHO$. *Bromochloral.* (126°). S.G. ^{15} 1·9176. Prepared by the action of bromine on di-chloro-acetal $CHCl_2.CH(OEt)_2$ (Jacobsen a. Neumeister, *B.* 15, 600). Colourless pungent liquid. On heating with H_2SO_4 it gives bromochloralide $C_4H_2Cl_4Br_2O_3$ [122°].

Hydrate $CCl_2Br.CH(OH)_2$. *Di-chloro-bromo-acetic orthaldehyde.* [51°]. Colourless trimetric plates. Sol. water, alcohol, and ether.

Alcoholate $CCl_2Br.CH(OH)(OEt)$: [43°]; slender needles.

CHLORO-BROMO-ACETO-ACETIC ETHER $C_6H_8ClBrO_3$. From chloro-aceto-acetic ether and Br; or from bromo-aceto-acetic ether and Cl (Merves, *A.* 245, 62). Oil. NaOEt gives bromo-acetic ether.

Chloro-di-bromo-aceto-acetic ether $C_6H_6ClBr_2O_3$. From di-bromo-aceto-acetic ether and Cl in diffused daylight (M.). NaOEt forms chloro-bromo-acetic ether (162°).

Di-chloro-bromo-aceto-acetic ether $C_6H_6Cl_2BrO_3$. From bromo-aceto-acetic ether and Cl (M.). NaOEt forms di-chloro-acetic ether.

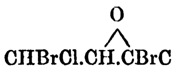
Di-chloro-di-bromo-aceto-acetic ether $C_6H_6Cl_2Br_2O_3$ *i.e.* $CHBr_2.CO.CCl_2.CO_2Et$(?) S.G. $\frac{19}{14}$ 1·956. Formed by bromination of di-chloro-aceto-acetic ether. Oil. On saponification by heating with HCl it yields di-chloro-di-bromo-acetone (Conrad a. Guthzeit, *B.* 16, 1551).

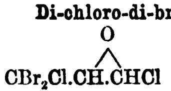
CHLORO-BROMO-ACETONE C_2H_3ClBrO *i.e.* $CH_2Cl.CO.CH_2Br$ or $CH_2Cl.\overbrace{CH.CH}^{O}Br$. [35°]. (c. 179°). Obtained from epichlorhydrin $CH_2Cl.\overbrace{CH.CH}^{O}{}_2$ by treatment with HBr and oxidation of the resulting $CH_2Cl.CH(OH).CH_2Br$ (Theegarten, *B.* 6, 897, 1276). Pungent crystals, sl. sol. water; v. sol. alcohol and ether. Forms a crystalline compound with $NaHSO_3$ (Theegarten; *cf.* Cloez, *A. Ch.* [6] 9, 145).

Chloro-tri-bromo-acetone $C_3H_2Br_3ClO$. [50°]. Prepared by heating dichloro-dibromo-acetone with HBr; or dichlorhydrin (1 mol.) with bromine (3 mols.) and water at 110° (Claus a. Lindhorst, *B.* 13, 1210). Trimetric prisms: $a:b:c$ = ·7124:1:2.

Chloro-tri-bromo-acetone $C_3H_2ClBr_3O$. *Tri-bromo-epichlorhydrin.* Prepared by treating epichlorhydrin (1 mol.) with bromine (1 mol.) at 100°. Pungent liquid; heavier than water; cannot be distilled even *in vacuo*. On shaking with water it forms a hydrate $C_3H_2ClBr_3O$ 4aq [55°] (Grimaux a. Adam, *Bl.* [2] 33, 257; *cf.* Cloez, *A. Ch.* [6] 9, 145).

Chloro-tri-bromo-acetone $C_3H_2ClBr_3O$ *i.e.* $CBr_3.CO.CH_2Cl$. (215°). S.G. 2·27. From chloro-acetone and bromine at 100° (Cloez). Pungent liquid. Forms hydrates $C_3H_2ClBr_3O$ 4aq (from water) and $C_3H_2ClBr_3O$ aq (from alcohol). Cold aqueous ammonia forms bromoform and chloro-acetamide.

Di-chloro-di-bromo-acetone $C_3H_2Cl_2Br_2O$ *i.e.*  $CHBrCl.\overbrace{CH.C}^{O}BrCl$ or $CHBrCl.CO.CHBrCl$. [-8°]. (135°) at 40 mm. From di-chloro-acetone (derived from epichlorhydrin) and bromine (Cloez). Does not combine with $NaHSO_3$. With water it forms long prisms of the hydrate $C_2H_2Cl_2Br_2O$ 4aq [54°]. Does not give off a chloro-bromo-methane when treated with ammonia.

Di-chloro-di-bromo-acetone $C_3H_2Cl_2Br_2O$ *i.e.*  $CBr_2Cl.\overbrace{CH.CH}^{O}Cl$ or $CBr_2Cl.CO.CH_2Cl$ (141°) at 20 mm. Prepared by heating dichlorhydrin (1 mol.) with bromine (3 mols.) and ½ the volume of water to 110° until the colour of the Br has gone; the yield is theoretical (Claus a. Lindhorst, *B.* 13, 1209; *cf.* Carius, *A.* 155, 38; Grimaux a. Adam, *Bl.* [2] 32, 14; Cloez, *loc. cit.*). Forms a hydrate $C_3H_2Cl_2Br_2O$ 4aq, [56°], (140°-150°) at 20 mm. Not identical with the preceding (C.).

Di-chloro-di-bromo-acetone $CHCl_2.CO.CHBr_2$. (120°) at 25 mm. Formed by the action of bromine on ordinary di-chloro-acetone or Barbaglia's di-chloro-acetone (170°) (Cloez). It forms unstable hexagonal tables of $C_3H_2Cl_2Br_2O$ 4aq. Ammonia forms no chloro-bromo-methane. $HgCl_2$ gives tetra-chloro-acetone.

Di-chloro-di-bromo-acetone $C_3H_2Cl_2Br_2O$ or $CHCl_2.CO.CHBr_2$ (?) Formed by heating di-chloro-di-bromo-aceto-acetic ether with HCl (Conrad a. Guthzeit, *B.* 16, 1552). Colourless pungent liquid. Forms a hydrate $C_3H_2Cl_2Br_2O$ 4aq crystallising in large colourless six-sided tables. Is perhaps identical with the preceding.

Di-chloro-tetra-bromo-acetone $CClBr_2.CO.CClBr_2$. [79°]. Formed by the action of bromine upon *p*-di-chloro-*p*-di-oxy-quinone (chloranilic acid) $C_6Cl_2(OH)_2O_2$. Transparent monoclinic crystals (from acetic acid). Heated with baryta-water it yields chloro-di-bromo-methane $CHClBr_2$. Dry NH_3 gas converts it into chloro-di-bromo-acetamide $CClBr.CONH_2$ and chloro-di-bromo-methane. With phenyl-hydrazine it gives a mixture of chloro- and bromo-benzene (Levy a. Jedlička, *B.* 20, 2319; *cf.* Stenhouse, *A. Suppl.* 8, 17).

Tri-chloro-bromo-acetone $C_3H_2Cl_3BrO$ *i.e.* $CCl_3.CO.CH_2Br$. (190°). From tri-chloro-acetone and bromine at 100°. Very hygroscopic, forming hexagonal tables of the hydrate $C_3H_2Cl_3BrO$ 4aq [48°]. With ammonia it forms chloroform and bromo-acetamide (Cloez).

TRI-CHLORO-αβ-DI-BROMO-ACETYL-PROPIONIC ACID $C_5H_3Cl_3Br_2O_3$ *i.e.* $CCl_3.CO.CHBr.CHBr.CO_2H$. [98°]. From tri-chloro-acetyl-acrylic acid and Br in chloroform (Kekulé a. O. Strecker, *A.* 223, 188). Volatile with steam; may be sublimed; insol. cold water. Boiling lime-water splits it up into chloroform and inactive tartaric acid.

CHLORO-BROMO-ACRYLIC ACID $C_3H_2ClBrO_2$ *i.e.* $CBrCl:CH.CO_2H$ (?) [70°]. S. 5·75 at 20°. Prepared by the action of HCl on bromo-propiolic acid at 0° (Mabery a. Lloyd, *Am.* 3, 127; Hill, *B.* 12, 660). Needles or prisms; may be sublimed. V. sol. alcohol and ether. Chlorine forms tri-chloro-bromo-propionic acid [84°] (Mabery, *Am.* 9, 1).

Salts.—KA′.—BaA'_2 2aq: flattened prisms. S. 14·15 at 20°.—CaA'_2 4aq: needles; v. e. sol. hot water.—AgA′.

(α)-Chloro-di-bromo-acrylic acid $C_2ClBr_2.CO_2H$ *i.e.* $CBr_2:CCl.CO_2H$ (?) [104°]. S. 5·7 at 20°. Prepared by the action of ClBr in chloroform on bromo-propiolic acid in the cold (Mabery a. Lloyd, *Am.* 6, 157). Triclinic prisms (from CS_2); v. sol. hot water, CS_2, and chloroform.

Salts.—AgA′: trimetric plates (from water); not affected by light.—CaA'_2 2½aq: branching needles.—BaA'_2 3aq: flat prisms. S. 26 at 20°.

(β)-Chloro-di-bromo-acrylic acid $CBrCl:CBr.CO_2H$. [99°]. S. 2·5 at 20°. From chloro-tri-bromo-acrylic acid by adding baryta-water in the cold till alkaline (M. a. L.). Prisms (from CS_2); v. sol. alcohol, ether, and hot water.—BaA'_2 3aq: slender prisms. S. 35 at 20°.—CaA'_2 4aq: branching needles.

Di-chloro-bromo-acrylic acid $C_2BrCl_2.CO_2H$ *i.e.* $CCl_2:CBr.CO_2H$(?) [78°–80°]. S. 6·9 at 20°. Obtained by the action of cold baryta-water on di-chloro-di-bromo-propionic acid obtained from αβ-di-bromo-acrylic acid and chlorine (Mabery, *Am.* 9, 8). Prisms; v. sol. alcohol and ether: sl. sol. cold CS_2.

Salts.—KA′: slender needles.—AgA′: slender needles.—BaA'_2 3aq: trimetric plates.—CaA'_2 4aq: pearly needles.

Di-chloro-bromo-acrylic acid $C_2BrCl_2.CO_2H$ *i.e.* $CClBr:CBr.CO_2H$(?) [85°]. S. 2·6 at 20°. Obtained by the action of cold baryta-water (1 mol.) on di-chloro-di-bromo-propionic acid (1 mol.) that has been prepared from bromine and αβ-di-chloro-acrylic acid (M.). Prisms; v. sol. alcohol and ether, m. sol. CS_2. This acid is possibly identical with the preceding.

Salts. KA′: pearly needles.—AgA′: slender needles.—BaA'_2 3aq: trimetric plates.—CaA'_2 4aq: jagged plates.

CHLORO-BROMO-ALDEHYDE *v.* CHLORO-BROMO-ACETIC ALDEHYDE

ω-DI-CHLORO-*m*-BROMO-AMIDO-ACETOPHENONE [5:2:1] $C_6H_3Br(NH_2).CO.CHCl_2$. [110°–120°]. Formed by boiling *ωωm*-tri-bromo-amido-acetophenone with HCl (Baeyer a. Bloem, *B.* 17, 967). Sublimable. Fine felted orange needles or long flat prisms. V. sol. alcohol, sl. sol. water. By boiling with dilute NaOH and exposure to the air it yields bromo-indigo.

CHLORO-BROMO-ANILINE $C_6H_3ClBr(NH_2)$ [2:4:1]. [69°]. Formed, together with *p*-bromo-aniline, by the action of tin and HCl on *p*-bromo-nitro-benzene (Hubner a. Alsberg, *A.* 156, 312; Fittig a. Buchner, *A.* 188, 14). Formed also by chlorinating *p*-bromo-aniline. Prisms; volatile with steam. B′HCl.

Chloro-di-bromo-aniline $C_6H_2ClBr_2(NH_2)$ [6:4:2:1]. [95°]. Formed by bromination of *o*-chloro-aniline (Langer, *B.* 15, 1065; *A.* 215, 115). Long white needles (from benzoline); v. sol. boiling alcohol and ether.

Chloro-di-bromo-aniline $C_6H_2ClBr_2(NH_2)$. Formed by brominating *p*-chloro-aniline (Hofmann, *A.* 53, 38). White prisms, which melt in hot water; volatile with steam. Does not form salts.

Chloro-tri-bromo-aniline $C_6HClBr_3(NH_2)$ [3:2:4:6:1]. [124°]. Formed by bromination of *m*-chloro-aniline by Br in dilute HCl (Langer, *B.* 15, 1065; *A.* 215, 112). Thin white needles (from alcohol); v. sol. boiling alcohol and ligroin.

Di-chloro-bromo-aniline $C_6H_2Cl_2Br(NH_2)$ [2:6:4:1]. [93·5°]. Formed by chlorinating *p*-bromo-aniline (Fittig a. Buchner, *A.* 188, 22). Does not unite with acids.

Di-chloro-tri-bromo-aniline $C_6Cl_2Br_3(NH_2)$ [3:5:2:4:6:1]. [219·5°]. From di-chloro-aniline $C_6H_3(NH_2)Cl_2$ [1:3:5] in dilute HCl by bromine-water (Langer, *A.* 215, 122). White needles (from alcohol). M. sol. boiling alcohol.

Tri-chloro-di-bromo-aniline $C_6Cl_3Br_2(NH_2)$ [2:4:6:3:5:1]. [238·5°]. From $C_6H_3(NH_2)Br_2$ [1:3:5] in acetic acid by Cl (Langer, *A.* 215, 118). White needles (from alcohol).

DI-CHLORO-BROMO-ANTHRACENE $C_{14}H_7Cl_2Br$. [168°]. Formed by heating di-chloro-anthracene tetra-bromide at 190° (Schwarzer, *B.* 10, 376). Small greenish-yellow laminæ; v. sol. benzene and chloroform.

Di-chloro-di-bromo-anthracene $C_{14}H_6Cl_2Br_2$. [252°]. From di-chloro-anthracene tetrabromide and alcoholic KOH (S.). Small yellow needles (from benzene); sl. sol. alcohol, v. sol. benzene.

Di-chloro-tetra-bromo-anthracene $C_{14}H_4Cl_2Br_4$. Formed by the action of alcoholic KOH upon di-chloro-di-bromo-anthracene-tetrabromide (Hammerschlag, *B.* 19, 1107). Golden-yellow needles. Solid at 380°. V. sl. sol. all solvents. By CrO_3 and acetic acid it is oxidised to tetra-bromo-anthraquinone.

DI-CHLORO-DI-BROMO-ANTHRACENE-TETRA-BROMIDE $C_{14}H_6Cl_2Br_6$. [212°]. Glistening white needles (from acetic acid). Formed by combination of di-chloro-di-bromo-anthracene with bromine vapour. By alcoholic KOH it is converted into di-chloro-tetra-bromo-anthracene (Hammerschlag, *B.* 19, 1107).

m-**CHLORO-BROMO-BENZENE** C_6H_4ClBr [1:3]. From *p*-chloro-aniline by bromination and elimination of NH_2 by the diazo-reaction (Korner, *J.* 1875, 326; *G.* 4, 305).

p-**Chloro-bromo-benzene** C_6H_4ClBr [1:4]. [67°]. (196°). From *p*-bromo-aniline by displacement of NH_2 by Cl; or from *p*-chloro-aniline by displacing NH_2 by Br (Griess, *Tr.* 1864 [3] 702). Also by boiling *p*-chloro-benzene with bromine (Körner, *G.* 4, 342).

Chloro-tri-bromo-benzene $C_6H_2ClBr_3$ [1:2:4:6]. [80°] (S.); [82°] (L.). *Formation.*—1. By heating the perbromide of tri-bromo-diazo-benzene chloride (from tri-bromaniline) with glacial acetic acid (Silberstein, *J. pr.* [2] 27, 113).— 2. From $C_6HClBr_3(NH_2)$ [123·5°], alcohol, and amyl nitrite at 100° (Langer, *A.* 215, 113; *B.* 15, 1065). *Properties.*—Long satiny needles. Insol. water, sl. sol. cold alcohol and glacial acetic acid, v. sol. hot alcohol, hot glacial acetic acid, ether, benzene and $CHCl_3$.

Di-chloro-di-bromo-benzene $C_6H_2Br_2Cl_2$. [67°] (Garzino, *G.* 17, 502).

Di-chloro-tri-bromo-benzene $C_6HCl_2Br_3$ [1:3:2:4:6]. [121°]. From $C_6(NH_2)Cl_2Br_3$ by treatment with amyl nitrite and alcohol (Langer, *A.* 215, 120; *B.* **15**, 1332). Small thin needles (from alcohol).

Tri-chloro-di-bromo-benzene $C_6HCl_3Br_2$ [1:3:5:2:4]. [119°]. From $C_6(NH_2)Cl_3Br_2$ and amyl nitrite in alcohol (Langer, *A.* 215, 119). Slender needles. V. sol. boiling alcohol.

CHLORO-BROMO-BENZOIC ACID $C_7H_4ClBrO_2$ *i.e.* $C_6H_3ClBr.CO_2H$. [151°]. S. ·26 at 21°. Formed by adding bromine to a hot solution of silver *o*-chloro-benzoate (but not of the free acid) (Pfeifer, *B.* **5**, 656). Slender needles (from water); may be sublimed.—KA′aq.—BaA′$_2$ 3aq.—CaA′$_2$ 2aq.

Chloro-bromo-benzoic acid $C_6H_3ClBr.CO_2H$. S. ·09 at 21°. From *m*-chloro-benzoic acid and bromine (P.). Slender needles.—BaA′$_2$ 2aq.

DI-CHLORO-DI-BROMO-BUTANE $C_4H_6Cl_2Br_2$ *i.e.* $CH_3.CHBr.CHBr.CHCl_2$. From Br and the di-chloro-butylene derived from crotonic aldehyde (Kekulé, *A.* 162, 98; Newbury, *Am.* 5, 113). Decomposes above 100°. Converted by boiling dilute K_2CO_3 into C_4H_6ClBrO (115°–120°).

CHLORO-DI-BROMO-BUTYL ALCOHOL $C_4H_7ClBr_2O$. Obtained by the union of bromine with chloro-butenyl (chloro-crotyl) alcohol which is itself got by reduction of tri-chloro-butyl alcohol (Garzarolli-Thurnlackh, *A.* **213**, **378**). HNO_3 oxidises it to chloro-di-bromo-butyric acid.

CHLORO-DI-BROMO-BUTYRIC ACID $C_4H_5ClBr_2O_2$ *i. e.* $CH_3.CHBr.CClBr.CO_2H$ (?) [92°]. From α-chloro-crotonic acid and Br (Sarnoff, *A.* 164, 105). Prisms, m. sol. cold, decomposed by hot, water. Distillation, or treatment with zinc and HCl, converts it into chloro-crotonic acid. –PbA′$_2$.—AgA′.

Chloro-tri-bromo-butyric acid $C_4H_4ClBr_3O_2$. [140°]. Formed by oxidising the corresponding aldehyde with fuming HNO_3 (Pinner, *B.* 8, 1324). Small plates.

CHLORO-DI-BROMO-BUTYRIC ALDEHYDE $C_4H_5ClBr_2O$ *i. e.* $CH_3.CHBr.CClBr.CHO$. From Br and α-chloro-crotonic aldehyde in the cold (Pinner, *B.* 8, 1322). Oil; with water it slowly forms a solid **hydrate** or orthaldehyde $C_4H_5ClBr_2(OH)_2$.

Chloro-tri-bromo-butyric aldehyde $C_4H_4ClBr_3O$. Formed by warming α-chloro-crotonic aldehyde with bromine (P.). Oil. Forms a **hydrate** or orthaldehyde $C_4H_4ClBr_3(OH)_2$ [78°] crystallising in slender needles.

Di-chloro-di-bromo-butyric aldehyde $CH_2Cl.CHBr.CClBr.CHO$. [c. –78°]. From αγ-di-chloro-crotonic aldehyde and Br in the cold (Natterer, *M.* 4, 540). Combines with $NaHSO_3$. It forms a crystalline **hydrate** or orthaldehyde $CH_2Cl.CHBr.CClBr.CH(OH)_2$ [72°].

CHLORO-BROMO-CAMPHOR *v.* CAMPHOR.

CHLORO-DI-BROMO-*n*-CUMENE $C_6H_5CHBr.CHBr.CH_2Cl$. [96·5°]. From styryl chloride and Br. Tables (from ether).

TRI-CHLORO-BROMO-CYMENE $C_6Cl_3Br(CH_3)(C_3H_7)$(?) [65°]. From sodium tri-chloro-cymene sulphonate and bromine-water (Kelbe, *B.* 16, 619). Needles.

CHLORO-PENTA-BROMO-DECYLENE $C_{10}H_{14}ClBr_5$. From Br and menthyl chloride (Oppenheim, *A.* 130, 177).

s-**CHLORO-BROMO-ETHANE** $CH_2Cl.CH_2Br$. *Ethylene chloro-bromide.* (108°). S.G. $\frac{0}{0}$ 1·79; $\frac{10}{0}$ 1·70.

Formation.—1. From *s*-chloro-iodo-ethane and Br (Henry, *A.* 156, 14).—2. From ethylene di-bromide and $HgCl_2$ (Montgolfier a. Giraud, *Bl.* [2] 33, 12).—3. From $CH_2Cl.CH_2.OH$ and Br at 130° (Demole, *B.* 9, 556).—4. From ethyl bromine by chlorination (Lescœur, *Bl.* [2] 29, 484).

Preparation.—1. Bromine (500 g.) is dissolved in 700 c.c. HCl mixed with 700 c.c. water, cooled with ice, and treated with chlorine as soon as the temperature of the liquid has fallen to 2°. The chlorine is passed in, with frequent shaking, until the colour of the bromine has disappeared. Ethylene is then passed in, and the oil washed, dried, and distilled. It boils at 107°–109°. If it boils at 109°–111° it contains ethylene bromide (M. Simpson, *Pr.* **27**, 119; J. W. James, *J. pr.* [2] 26, 380; *C. J.* 43, 37).—2. $C_2H_4Br_2$ is gently warmed with $SbCl_5$, the product poured into strong HCl, and the oil washed with very dilute NaOH and distilled (Lössner, *J. pr.* 121, 421; James, *C. J.* 35, 806).

Reactions.—1. Acts upon boiling alcoholic KCNS forming $C_2H_4Cl(CNS)$.—2. Alcoholic KOH gives KBr and chloro-ethylene.

***u*-Chloro-bromo-ethane** $CH_3.CHClBr$. *Ethylidene-chloro-bromide.* (82°) (R.); (83° i. V.) (S.). S.G. $\frac{14}{}$ 1·61 (R.); $\frac{10}{}$ 1·67.

Formation.—1. From bromo-ethylene and conc. HClAq at 100° (Reboul, *A.* 155, 215). 2. By brominating ethyl chloride in sunlight (Staedel, *B.* 11, 1739; Denzel, *A.* 195, 193).—3. By chlorinating ethyl bromide (Lescœur, *Bl.* [2] 29, 483).

Properties.—Oil. Converted by alcoholic KOH into KBr and bromo-ethylene. Ag_2O gives aldehyde.

Chloro-di-bromo-ethane $CH_3.CBr_2Cl$. (124° i. V.). S.G. $\frac{16}{}$ 2·134. A product of bromination of ethyl chloride in sunlight (Staedel, *B.* 11, 1739; Denzel, *A.* 195, 196). Liquid. Converted by alcoholic KOH into $CH_2:CClBr$.

Chloro-di-bromo-ethane $CH_2Br.CHClBr$. (163° i. V.). S.G. $\frac{16}{}$ 2·268. From chloro-ethylene and Br (Hugo Müller, *A. Suppl.* 3, 287). From chloro-bromo-iodo-ethane and Br (Henry, *Bl.* [2] 42, 263). Also from EtCl and Br in sunlight (S.; D.). Oil. Alcoholic KOH gives $CH_2:CClBr$. With $SbCl_5$ it gives $CH_2Br.CHCl_2$.

Chloro-di-bromo-ethane $CH_2Cl.CHBr_2$. From crude chloro-bromo-iodo-ethane and Br (H.). Alcoholic KOH gives $CH_2:CBr_2$ (89°) and $CH_2:CBrCl$ (63°).

Chloro-tri-bromo-ethane $CH_2Br.CClBr_2$. (201° i. V.) at 735 mm. S.G. $\frac{16}{}$ 2·602. Formed by the action of bromine on $CH_3.CClBr_2$, on ethyl chloride, on $CH_2Br.CHBrCl$, or on $CH_2:CClBr$ (S.; D.; H.). Gives $CHBr:CBrCl$ with alcoholic KOH. $SbCl_5$ forms $CH_2Br.CCl_3$.

Chloro-tetra-bromo-ethane $CHBr_2.CBr_2Cl$. *Chloro-acetylene tetra-bromide.* [33°]. (240°) at 735 mm. S.G. $\frac{16}{}$ 3·366. From EtCl and Br in sunlight (S.; D.). From chloro-acetylene and bromine (Wallach, *A.* 203, 89). Also from chloro-di-bromo-ethylene and Br (Mabery, *Am.* 5, 255). Pungent crystals; v. e. sol. alcohol and ether.

Chloro-penta-bromo-ethane C_2ClBr_5. [170°]. Prepared by the action of bromine on chloro-tribromo- and chloro-tetrabromo-ethane (Denzel, *B.* 12, 2207).

Di-chloro-bromo-ethane $CH_3.CCl_2Br$. (99° i. V.). S.G. $\frac{16}{}$ 1·752. Formed by brominating ethylidene chloride in sunlight (S.; D.). Liquid.

Di-chloro-bromo-ethane $CHCl_2.CH_2Br$. (138°). S.G. 1·859. From $CHCl_2.CH_2OH$ and PBr_3 (Lacre, *C. R.* 104, 1186). From $CHBr_2.CH_2Br$ (Henry, *C. R.* 97, 1491; *Bl.* [2] 42, 262), or $CHClBr.CH_2Br$ and $SbCl_5$. Converted by alcoholic KOH into $CH_2:CCl_2$.

Di-chloro-bromo-ethane $CHClBr.CH_2Cl$. (140° cor.). S.G. $\frac{15}{15}$ 1·8685; $\frac{25}{25}$ 1·8542. M.M. 10·995 at 21·6°. Formed by gradually adding bromo-ethylene to chloroform through which a current of chlorine is passing (Perkin, *C. J.* 45, 535).

According to Lescœur (*Bl.* [2] 29, 485) three isomeric di-chloro-bromo-ethanes are formed by chlorinating ethyl bromide, viz.: (1). (137°); S.G. $\frac{0}{}$ 1·88,—(2). (151°); S.G. $\frac{0}{}$ 1·998,—(3). (c. 160°); S.G. $\frac{0}{}$ 2·113.

Di-chloro-di-bromo-ethane $CHCl_2.CHBr_2$. *Acetylene di-chloro-di-bromide.* (195°–200°). S.G. $\frac{12}{}$ 2·391. From acetylene dibromide and $SbCl_5$ in the cold (Sabanejeff, *A.* 216, 256). Also from acetylene, Br (81 g.), and (120 g. of) aqueous HClO. *Reactions.*—1. Converted by Zn and alcohol into chloro-bromo-ethylene (*q. v.*).—2. Boiled 6 hours with alcoholic KOAc it forms $CHBr:CCl_2$ [114°-116°].

***s*-Di-chloro-di-bromo-ethane** $CHClBr.CHClBr$. *Acetylene di-chloro-di-bromide.* (190°-195°). From bromine and acetylene di-chloride; or from chlorine and acetylene di-bromide (Sa.). Gives, with zinc and alcohol, acetylene dichloride (50°–60°).

Di-chloro-di-bromo-ethane $CH_2Br.CBrCl_2$. (177°). S.G. $\frac{16}{}$ 2·270. From $CH_3.CHCl_2$ and Br in sunlight (S.; D.).

Di-chloro-tri-bromo-ethane $CHBr_2.CBrCl_2$. (215°–220°). From $CH_3.CHCl_2$ and Br in sunlight (S.; D.).

Di-chloro-tetra-bromo-ethane $C_2Cl_2Br_4$ *i.e.* $CBr_3.CCl_2Br$. [180°]. Colourless crystals. Prepared by the action of bromine on $CH_2Br.CCl_2Br$ (Denzel, *B.* 12, 2207).

Tri-chloro-bromo-ethane $CCl_3.CH_2Br$. (152°). S.G. $\frac{0}{0}$ 1·884. Formed by heating tri-chloro-ethane $CCl_3.CH_3$ with bromine at 160°; or by the action of $SbCl_5$ on $CCl_2Br.CH_2Br$ or $CClBr_2.CH_2Br$. Converted by alcoholic KOH into $CCl_2:CHBr$ (115°) (Henry, *C. R.* 98, 370).

Tri-chloro-di-bromo-ethane $CHBr_2.CCl_3$. (200°). S.G. $\frac{0}{}$ 2·317. From chloral and PCl_3Br_2 (Paterno, *J.* 1871, 512; *G.* 1, 590).

Tetra-chloro-di-bromo-ethane $CCl_2Br.CCl_2Br$. *Bromide of per-chloro-ethylene.* S.G. $\frac{21}{}$ 2·3. From C_2Cl_4 and Br in sunshine (Malaguti, *A. Ch.* [3] 16, 14). Tables (from alcohol). Begins to volatilise at 100° but decomposes at 200° into Br and C_2Cl_4.

Tetra-chloro-di-bromo-ethane $CCl_3.CClBr_2$. From penta-chloro-ethane and Br at 200° (Paterno, *G.* 1, 593). Also from $CHBr_2.CHBr_2$ and chlorine (Bourgoin, *Bl.* [2] 23, 4). Prisms (from alcohol); smells like camphor. May be sublimed, but decomposed by heat into chlorine and $C_2Cl_2Br_2$.

CHLORO-BROMO-ETHER *v.* CHLORO-BROMO-DI-ETHYL OXIDE.

***s*-CHLORO-BROMO-ETHYLENE** C_2H_2ClBr *i.e.* $CHCl:CHBr$. *Acetylene chloro-bromide.* (82°). S.G. $\frac{0}{}$ 1·8157 (P.); 1·779 (S.); $\frac{20}{}$ 1·747 (S.). Bromine (2 mols.) is slowly added to acetylene chloro-iodide under water. The liberated iodine is removed by $Na_2S_2O_3$. The yield is small (Plimpton, *C. J.* 41, 393). Formed also by treating $CHCl_2.CHBr_2$ with zinc and alcohol (Sabanejeff, *A.* 216, 258). Liquid, does not polymerise. With alcoholic KOH it gives off an explosive gas, probably C_2HCl.

Chloro-bromo-ethylene $CH_2:CClBr$. (62°). From chloro-ethylene bromide $CH_2Br.CHClBr$ and KCy (Hugo Müller, *C. J.* 17, 420) or alcoholic KOH (Denzel, *A.* 195, 206; Demole a. Durr, *B.* 11, 1302). Also from chloro-bromo-iodo-ethane (from C_2H_3Br and ICl) by alcoholic KOH (Henry, *Bl.* [2] 42, 263). Pungent odour, readily polymerises, becoming solid. Absorbs dry oxygen forming chloro-acetyl bromide and bromo-acetyl chloride.

Chloro-di-bromo-ethylene $CHBr:CBrCl$. (142°) at 735 mm. S.G. $\frac{16}{}$ 2·275 (S.). From chloro-tri-bromo-ethane $CH_2Br.CBr_2Cl$ and alcoholic KOH (Staedel, *B.* 11, 1740). Formed also by boiling chloro-tri-bromo-propionic acid with baryta-water (Mabery, *Am.* 5, 255). Liquid.

Chloro-tri-bromo-ethylene C_2ClBr_3 *i.e.* $CBr_2:CBrCl$. [34°]. (104°) at 730 mm. Prepared by the action of alcoholic KOH on chloro-tetra-bromo-ethane (Denzel, *B.* 12, 2208).

Di-chloro-bromo-ethylene $CHBr:CCl_2$. [114°–116°]. S.G. $\frac{16}{}$ 1·906. Formed by the action of alcoholic KOH on $CH_2Br.CBrCl_2$ (Denzel, *A.* 195, 206), or on $CCl_3.CH_2Br$ (Henry, *C. R.* 98, 370). Also from $CHBr_2.CHCl_2$ by alcoholic KOAc (Sabanejeff, *A.* 216, 261).

Di-chloro-di-bromo-ethylene $CCl_2:CBr_2$. (c. 194°?). Prepared by the action of alcoholic KOH on di-chloro-tri-bromo-ethane $CHBr_2.CBrCl_2$ (Staedel, *B.* 11, 1740). Also from $CCl_3.CClBr_2$ by heating with aniline (Bourgoin, *Bl.* [2] 24, 116). Solidifies below 0°.

CHLORO-DI-BROMO-DI-ETHYL OXIDE $CHClBr.CHBr.OEt$. (170°–180°). From chloro-vinyl ethyl oxide and Br (Godefroy, *C. R.* 102, 869).

Tri-chloro-di-bromo-di-ethyl oxide $C_4H_5Cl_3Br_2O$ *i.e.* $CCl_2Br.CClBr.OEt$. [17°]. From tri-chloro-vinyl ethyl oxide and Br (Busch, *B.* 11, 446). With AgOAc it gives $C_2Cl_2Br(OAc)_2.OEt$ (180°–190°).

Hexa-chloro-tetra-bromo-di-ethyl oxide $C_4Cl_6Br_4O$. [96°]. Obtained by union of Br with chloroxethose C_4H_6O, a substance formed by the action of alcoholic K_2S on perchlorinated ether (Malaguti, *A. Ch.* [3] 16, 19).

DI-CHLORO-TETRA-BROMO-FLUORESCEÏN $C_{20}H_6O_5Cl_2Br_4$ *i.e.* $C_6H_2Cl_2(C_2O_2)(C_6HBr_2OH)_2O$. *Di-chloro-eosin.* Formed by brominating di-chloro-fluorescein (from resorcin and di-chloro-phthalic anhydride). The alkaline solution has a bluer shade than that of eosin (Le Royer, *A.* 238, 358).

Salt.—$C_{20}H_4K_2O_5Cl_2Br_4$.

CHLORO-BROMOFORM *v.* CHLORO-DI-BROMO-METHANE.

CHLORO-DI-BROMO-HEXANE $C_6H_{11}ClBr_2$. (219°). From hexenyl chloride and Br in CCl_4 (Destrem, *A. Ch.* [5] 27, 58).

Chloro-tetra-bromo-hexane $C_6H_9ClBr_4$. From Br and chloro-diallyl (Henry, *C. R.* 87, 171).

CHLORO-DI-BROMO-HEXYL ALCOHOL $C_6H_{11}ClBr_2O$. (c. 254°). S.G. $\frac{15}{}$ 1·99. From chloro-hexenyl alcohol (186°) and Br (Destrem, *A. Ch.* [5] 27, 58).

CHLORO-BROMHYDRIN *v.* CHLORO-BROMO-PROPYL ALCOHOL.

CHLORO-BROMO-HYDROQUINONE $C_6H_2ClBr(OH)_2$. [172°]. Formed by saponification of its di-acetyl-derivative produced by the action of acetyl bromide on chloro-quinone (Schulz, *B.* 15, 656). Formed also by the action of conc. HBrAq on chloro-quinone (Levy a. Schultz, *A.* 210, 160). Long needles. Sol. alcohol and ether, sl. sol. water. On oxidation it gives chloro-bromo-quinone [172°].

Di-acetyl-derivative $C_6H_2ClBr(OAc)_2$ [146°]. Short needles. Sol. alcohol and benzene.

Di-chloro-di-bromo-hydroquinone $C_6Cl_2Br_2(OH)_2$ [6:2:5:3:4:1]. [233°]. Formed by reduction of the corresponding quinone by $SnCl_2$ (Levy, *B.* 16, 1447; 18, 2369; Krause, *B.* 12, 54; Hantsch, *B.* 20, 2279). Monoclinic crystals: $a:b:c = 2·976:1:2·75$; $\beta = 77°\ 22'$.

Di-acetyl derivative $C_6Cl_2Br_2(OAc)_2$: [270°] (Levy, *B.* 18, 2369).

Tri-chloro-bromo-hydroquinone $C_6BrCl_3(OH)_2$ [229°]. From tri-chloro-bromo-quinone, HI, and phosphorus (Stenhouse, *A. Suppl.* 6, 219). Also from tri-chloro-quinone and conc. HBrAq (Levy a. Schultz, *A.* 210, 161). Monoclinic needles, $a:b:c = 2·915:1:2·671$; $\beta = 77°\ 40'$. Insol. water, sol. dilute alcohol.

CHLORO-BROMO-HYDROTHYMOQUINONE $C_6Me(C_3H_7)ClBr(OH)_2$ [3:6:2:5:4:1]. [63°] or [73°] (?). From chloro-thymoquinone $C_6HMe(C_3H_7)Cl(OH)_2$ [3:6:2:4:1] and HBr; or from bromo-thymoquinone $C_6HMe(C_3H_7)Br(OH)_2$ [3:6:2:5:1] [45°] and HCl. Obtained also by reducing chloro-bromo-thymoquinone [87°] with hydroxylamine (Schniter, *B.* 20, 1318). Needles.

Chloro-bromo-hydrothymoquinone $C_6Me(C_3H_7)ClBr(OH)_2$ [3:6:5:2:4:1]. [56°]. Formed by reducing chloro-bromo-thymoquinone [78°] with hydroxylamine (S.).

CHLORO-BROMO-HYDROTOLUQUINONE $C_6HMeClBr(OH)_2$. [123°] (anhy.). Formed by the action of HBr upon chloro-toluquinone. Crystals (containing aq). V. sol. alcohol and ether, m. sol. water and ligroin, sl. sol. benzene and chloroform (Schniter, *B.* 20, 2286).

Chloro-bromo-hydrotoluquinone $C_6HMeClBr(OH)_2$. [121°] (anhy.). Formed by the action of HCl upon bromo-toluquinone. Long needles, containing aq (from hot water). Begins to sublime at 105° (Schniter, *B.* 20, 2287).

CHLORO-BROMO-IODO-ACRYLIC ACID $C_2ClBrI.CO_2H$. [116°]. Formed by heating bromo-propiolic acid with an ethereal solution of ICl (Mabery a. Lloyd, *Am.* 4, 96; *P. Am. A.* 17, 99). Monoclinic prisms (from water) melting at 110°; but at 116° when crystallised from CS_2; may be sublimed.—AgA'.—CaA'_2 aq: branching needles.—$BaA'_2\ 3\frac{1}{2}$aq: prisms; S. 25·4 at 20°.

Chloro-bromo-iodo-acrylic acid $C_3HClBrIO_2$. [129°]. Glistening colourless plates. V. sol. water, alcohol, and ether. Formed by the action of a chloroform solution of ClBr upon iodo-propiolic acid (Stolz, *B.* 19, 539).

CHLORO-BROMO-IODO-ETHANE C_2H_3ClBrI. (194°). S.G. ^{0} 2·53. Slowly formed by union of ICl with bromo-ethylene in the cold (Maxwell Simpson, *A.* 136, 142; Henry, *C. R.* 98, 680). Oil. Converted by alcoholic KOH into KCl (3 pts.), KI (1 pt.), bromo-iodo-ethylene $CH_2:CBrI$, and chloro-bromo-ethylene $CH_2:CClBr$. Hence the chloro-bromo-iodo-ethane must be a mixture of isomerides.

CHLORO-BROMO-IODO-PROPANE C_3H_5ClBrI. S.G. ^{0} 2·325. From chloro-iodo-propyl alcohol and PBr_5 (Henry, *B.* 4, 702; *cf.* 3, 351). Oil.

DI-CHLORO-BROMO-MESITYLENE $C_9H_9BrCl_2$ *i.e.* $C_6H_2Br(CH_3)(CH_2Cl)_2$. [76°]. From bromo-di-ω-oxy-mesitylene by heating with conc. HClAq (Colson, *A. Ch.* [6] 6, 101). Readily gives off HCl in the air.

CHLORO-BROMO-METHANE CH_2ClBr. (68°). S.G. $\frac{19}{19}$ 1·991. V.D. 4·43. Formed by the action of excess of bromine on CH_2ClI (Henry, *C. R.* 101, 599). Oil; not decomposed by light.

Chloro-di-bromo-methane $CHClBr_2$. ***Chloro-bromoform.*** (119°) at 730 mm. (L. a. J.); (125°)

(J. a. N.). S.G. ^{15} 2·445. V.D. 7·37 (for 7·22). Occurs in crude bromine (Dyson, *C. J.* 43, 36). Formed by boiling di-chloro-tetra-bromo-acetone $CClBr_2.CO.CClBr_2$ with baryta-water. Prepared also by the action of NaOH on chloro-di-bromo-acetic aldehyde (Jacobsen a. Neumeister, *B.* 15, 601). Colourless liquid, of sweetish odour (Levy a. Jedlička, *B.* 20, 2319).

Di-chloro-bromo-methane $CHCl_2Br$. (92°). S.G. ^{15} 1·9254. *Bromochloroform.* Colourless liquid. Prepared by the action of NaOH on di-chloro-bromo-acetic aldehyde (Jacobsen a. Neumeister, *B.* 15, 601).

Tri-chloro-bromo-methane $CBrCl_3$. (104°). S.G. $\frac{0}{4}$ 2·0550 (Thorpe, *C. J.* 37, 203). C.E. (0°-10°) ·001089; (0°-100°) ·0012065. S.V. 108·43.

Formation.—1. By heating $CCl_3.SO_2Br$ with alcohol at 100° (Loew, *Z.* 1869, 624).—2. By bromination of chloroform (Paterno, *G.* 1, 593; Friedel a. Silva, *Bl.* [2] 17, 538).—3. By action of bromine on potassic tri-chloro-acetate at 120° (van 't Hoff, *B.* 10, 678).

Properties.—Liquid, smelling like carbon tetrachloride.

CHLORO-BROMO-METHANE SULPHONIC ACID. Barium salt $(CHClBr.SO_3)_2Ba$. From chloro-sulpho-acetate of barium and bromine (Andreasch, *M.* 7, 170). Satiny plates.

CHLORO-BROMO-METHYL-ETHYL-GLYOXALINE $C_6H_8ClBrN_2$ *i.e.* $C_3ClBr(CH_3)(C_2H_5)N_2$. *Chloro-bromo-oxal ethyline.* From chloro-methyl-ethyl glyoxaline by treatment with Br in CS_2 followed by boiling water (Wallach, *A.* 214, 290; *B.* 10, 1193). Oil with narcotic odour. Solidifies with difficulty. Sl. sol. water. Not volatile. With Br it forms $C_6H_8ClBrN_2Br_2HBr$.

Salts.—B'HCl: prisms.—$(B'HCl)_2PtCl_4$.—B'_2AgNO_3.

CHLORO-BROMO-NAPHTHALENE $C_{10}H_6ClBr$ [1:4]. [115°]. From (α)-naphthylamine *p*-sulphonic acid by conversion into bromo-naphthalene sulphonic acid, and treatment of the latter with PCl_5 (Clève, *Bl.* [2] 26, 540).

Chloro-bromo-naphthalene $C_{10}H_6ClBr$. [119°]. Formed, together with the following, by the action of Br (1 mol.) on (α)-chloro-naphthalene (1 mol.), or of Cl on (α)-bromo-naphthalene (Guareschi a. Biginelli, *G.* 16, 152; *C. C.* 1887, 518). Thin plates. Oxidised by CrO_3 to chloro-phthalic acid [184°]. Possibly identical with the preceding.

Chloro-bromo-naphthalene $C_{10}H_6ClBr$. [67°]. (303° uncor.). Prepared as above. Needles (by sublimation). CrO_3 in acetic acid gives chloro-bromo-naphthoquinone [167°] and chloro-bromo-phthalide.

Di-chloro-bromo-naphthalene $C_{10}H_7Cl_2Br$. [80°]. From di-chloro-naphthalene [38°] and Br in the cold (Laurent). Slender needles.

The following chloro-bromo-naphthalenes described by Laurent (*A. Ch.* 49, 218; 52, 275) are insufficiently characterised: $C_{10}H_4Cl_2Br_2$ (two), $C_{10}H_4Cl_3Br$ (three), and $C_{10}H_3Cl_3Br_2$ (two).

The following compounds are probably mixtures or molecular compounds: (*a*) $C_{20}H_9Cl_4Br_3$. [76°]. From di-chloro-naphthalene [38°] and Br followed by alcoholic KOH (Faust a. Saame, *A.* 160, 69). Needles (from ether-alcohol). (*b*) $C_{20}H_9Cl_4Br_3$. [73°]. From di-chloro-naphthalene [68°] by successive treatment with Br and alcoholic KOH (F. a. S.).

CHLORO-BROMO-NAPHTHALENE TETRA-BROMIDE $C_{10}H_6ClBr_5$. [110°]. From chloro-naphthalene and Br (Laurent). Triclinic columns.

CHLORO-DI-BROMO-NAPHTHALENE TETRA-CHLORIDE $C_{10}H_5ClBr_2Cl_4$. [150°]. From di-bromo-naphthalene tetra-chloride and chlorine. Triclinic columns, sl. sol. ether.

CHLORO-BROMO-NAPHTHOQUINONE $C_{10}H_4ClBrO_2$. [167°]. From chloro-bromo-naphthalene [67°] by CrO_3 in HOAc (Guareschi, *C. C.* 1887, 518).

CHLORO-BROMO-NITRO-ANILINE $C_6H_4ClBrN_2O_2$ *i.e.* $C_6H_2ClBr(NO_2)(NH_2)$ [4:6:2:1]. [106°]. From chloro-nitro-aniline in HClAq by bromine-vapour (Körner, *J.* 1875, 352; *G.* 4, 305). Orange-yellow needles.

CHLORO-BROMO-NITRO-BENZENE $C_6H_3ClBr(NO_2)$ [1:3:5]. [82·5°]. From the preceding by diazo- reaction (Körner, *G.* 4, 377). Laminæ.

Chloro-bromo-nitro-benzene $C_6H_3ClBr(NO_2)$ [1:4:2]. [69°]. From *p*-chloro-bromo-benzene and HNO_3 (K.).

Chloro-bromo-nitro-benzene $C_6H_3ClBr(NO_2)$ [1:3:4]. [49·5°]. From chloro-nitro-aniline [123°] by displacing NH_2 by Br (K.). With alcoholic NH_3 at 160° it regenerates the chloro-nitro-aniline.

TRI-CHLORO-DI-BROMO-NITRO-ETHANE $CCl_2Br.CClBr(NO_2)$. From $CCl_2{:}CCl(NO_2)$ and Br at 150°. Crystalline (Hoch, *J. pr.* [2] 6, 95).

CHLORO-BROMO-DI-NITRO-METHANE $CClBr(NO_2)_2$. Formed by passing chlorine into an aqueous solution of potassio-bromo-di-nitro-methane $CKBr(NO_2)_2$ (Losanitsch, *B.* 17, 848). Oil. V. sol. alcohol, insol. water. By caustic alkalis the Br atom is displaced by a metallic atom.

Chloro-di-bromo-nitro-methane $CClBr_2(NO_2)$. S.G. ^{15} 2·421. Formed by simultaneous action of bromine and potash on $CClH_2(NO_2)$ (Tscherniak, *B.* 8, 610). An oil, insol. potash, volatile with steam.

CHLORO-BROMO-NITRO-PHENOL $C_6H_2ClBr(NO_2)OH$ [4:2:6:1]. [125°]. From (4,6,1)-chloro-nitro-phenol [87°] and Br in HOAc in the cold (Ling, *C. J.* 51, 787). Converted by Br and water at 100° into tetra-bromo-quinone. $C_6H_2ClBrNO_3K$: dark red needles.—BaA'_2 aq.—CaA'_2 2½aq.

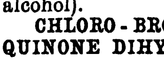
Chloro-bromo-nitro-phenol $C_6H_2ClBr(NO_2)OH$ [2:4:6:1]. [120°]. Formed by boiling (4,6,1)-chloro-nitro-phenol [87°] with Br and HOAc, an isomeric change taking place (L.). Formed also by chlorinating (4,6,1)-bromo-nitro-phenol [88°]. When heated with Br and water it gives chloro-tri-bromo-quinone.—$C_6H_2ClBrNO_3K$: red plates.—CaA'_2 7aq.

ω-TRI-CHLORO-*eso*-DI-BROMO-*eso*-DI-NITRO-DI-PHENYL-ETHANE

$CCl_3.CH(C_6H_3Br.NO_2)_2$.

[170°]. From $CCl_3.CH(C_6H_4Br)_2$ and fuming HNO_3 (Zeidler, *B.* 7, 1180). Needles (from alcohol).

CHLORO-BROMO-DI-OXY-(α)-NAPHTHO-QUINONE DIHYDRIDE $C_{10}H_6ClBrO_2$ *i.e.*



$$C_6H_4\left\langle\begin{array}{l}CO.C(OH)_2\\ \quad\;\;|\\ CO.CClBr\end{array}\right.$$

. [105°]. From bromo-oxy-

(α)-naphthoquinone and Cl in HOAc. Needles. Oxidation gives a body [141°] (Zincke a. Gerland, *B.* 20, 3216)

DI - CHLORO - DI - BROMO - TETRA - OXY-DIPHENYL $C_6HClBr(OH)_2.C_6HClBr(OH)_2$. [265°]. From di-chloro-tri-bromo-resorcin by successive treatment with $NaHSO_3$ and with tin and HCl (Benedikt, *M.* 4, 227).

CHLORO-BROMO-DI-OXY-QUINONE $C_6ClBr(OH)_2O_2$ [6:3:5:2:4:1] (Hantzsch a. Schniter, *B.* 20, 2279). From *m*-di-chloro-*m*-di-bromo-quinone and aqueous KOH (Krause, *B.* 12, 54) or tri-chloro-bromo-quinone (Levy, *A.* 210, 163; *B.* 16, 1444; *B.* 18, 2370). Red leaflets (containing aq); may be sublimed—K_2A''2aq.—Na_2A''2aq.—Ag_2A''.

CHLORO-DI-BROMO-OXY-VALERIC ACID $C_5H_7ClBr_2O_3$. [169°]. Prepared by the addition of Br to chloro-oxy-angelic acid (Pinner a. Klein, *B.* 11, 1497). Sol. ether, insol. benzene.

CHLORO-DI-BROMO-PENTANE $C_5H_9ClBr_2$. From isoprene hydrochloride C_5H_8HCl and Br (Bouchardat, *C. R.* 89, 1217).

Di-chloro-di-bromo-pentane $CH_3.CHBr.CBrCl.CHCl.CH_3$. (c. 143°) at 31 mm. From di-chloro-amylene $CH_3.CH{:}CCl.CHCl.CH_3$ and bromine (Thurnlackh, *A.* 223, 161).

Di-chloro-di-bromo-pentane $C_5H_8Cl_2Br_2$. (230°–240°). From di-chloro-amylene (146°) and Br (Pinner, *A.* 179, 35).

DI-CHLORO-BROMO-PHENOL $C_6H_2Cl_2Br(OH)$. [68°]. (268°) (Garzino, *C. C.* 1887, 1546). From (4,2,1)-di-chloro-phenol and Br. *Tri-chloro-bromo-phenol* $C_6HCl_3Br(OH)$. Bromine converts tri-chloro-phenol [67°] into $C_6H_2Cl_3BrO$ [99°]. This is perhaps $C_6H_2Cl_3(OBr)$; it is converted, by heating under water, into an isomeride, which is probably $C_6HCl_3Br(OH)$ (Benedikt, *M.* 4, 235).

TRI - CHLORO - DI - BROMO - DI - PHENYL-ETHANE $CCl_3.CH(C_6H_4Br)_2$. [141°]. From bromo-benzene (1 pt.), chloral (2 pts.), and H_2SO_4 (Zeidler, *B.* 7, 1180). Silky needles.

Di-chloro-di-bromo-di-phenyl-ethylene $CCl_2{:}C(C_6H_4Br)_2$. [120°]. Formed by the action of alcoholic KOH upon the preceding body (Zeidler, *B.* 7, 1180). Needles (from alcohol).

β-CHLORO-α-BROMO-β-PHENYL-PROPIONIC ACID $C_6H_5.CHCl.CHBr.CO_2H$. [182°]. From α-bromo-β-oxy-β-phenyl-propionic acid and conc. HClAq at 100° (Glaser, *A.* 147, 92). Monoclinic tables (from chloroform). Boiling water forms HCl and bromo-oxy-phenyl-propionic acid, together with a little phenyl-acetic aldehyde and ω-bromo-styrene.

α-Chloro-β-bromo-β-phenyl-propionic acid $C_6H_5.CHBr.CHCl.CO_2H$. [185°]. From α-chloro-β-oxy-β-phenyl-propionic acid and conc. HBrAq at 60° (G.). Monoclinic tables (from chloroform). Boiling water gives ω-chloro-styrene and a little chloro-oxy-phenyl-propionic acid, and phenyl-acetic aldehyde.

α-Chloro-αβ-di-bromo-β-phenyl-propionic acid $C_6H_5.CHBr.CBrCl.CO_2H$. [136°]. From α-chloro-β-phenyl-propionic acid and Br (Forrer, *B.* 16, 855). Tables (from water).

CHLORO-BROMO-PHTHALIDE $C_6H_2ClBr\Big\langle{}^{CH_2}_{CO}\Big\rangle O$. [179°]. Formed by oxidation of chloro-bromo-naphthalene [67°] with CrO_3 (Guareschi, *B.* 19, 1154).

CHLORO-BROMO-PICRIN *v.* CHLORO-DI-BROMO-NITRO-METHANE.

ω-CHLORO-α-BROMO-PROPANE C_3H_6ClBr *i.e.* $CH_3.CHBr.CH_2Cl$. *Propylene chloro-bromide.* (120°). Formed in small quantity, together with $CH_2Br.CH_2.CH_2Cl$ by treating allyl chloride with fuming HBr (Reboul, *A. Ch.* [5] 14, 487). Converted by alcoholic KOH into HCl and bromo-propylene.

α-Chloro-ω-bromo-propane $CH_3.CHCl.CH_2Br$. (120°). S.G. ^{0} 1·585. V.D. 5·52 (calc. 5·45). From propylene bromide by boiling with $HgCl_2$ (Friedel a. Silva, *Bl.* [2] 17, 532). Alcoholic KOH converts it into chloro-propylene (25°–30°).

Chloro-bromo-propane C_3H_6ClBr. (119°). From ClBr and C_3H_6 (Maxwell Simpson, *Pr.* 27, 119). Probably a mixture of the two preceding bodies.

ω-Chloro-β-bromo-propane $CH_2Br.CH_2.CH_2Cl$. *Tri-methylene chloro-bromide.* (142°). S.G. ^{8} 1·63. From tri-methylene bromide and $HgCl_2$. It is also the chief product of the union of HBr with allyl chloride (Reboul). Boiling alcoholic KOH gives ethyl-allyl oxide.

α-Chloro-α-bromo-propane $CH_3.CClBr.CH_3$. *Acetone chloro-bromide.* (c. 95°). S.G. ^{21} 1·474. From α-chloro-propylene $CH_3.CCl{:}CH_2$ and cold conc. HBrAq (Reboul, *A. Ch.* [5] 14, 482). Alcoholic KOH gives α-chloro-propylene and allylene.

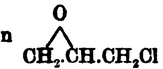
ω-Chloro-ω-bromo-propane $CH_3.CH_2.CHClBr$. (111°). S.G. ^{20} 1·59. From ω-chloro-propylene $CH_3.CH{:}CHCl$ and HBr (R.). Alcoholic KOH gives $CH_3.CH{:}CHCl$.

Chloro-di-bromo-propane $C_3H_5ClBr_2$. (198°). From allyl bromide and ClBr. They unite slowly in the cold (Maxwell Simpson, *Pr.* 27, 119).

ω-Chloro-ωα-di-bromo-propane $CH_3.CHBr.CHClBr$ (177° cor.). From $CH_3.CH{:}CHCl$ and Br (Reboul, *Bl.* [2] 26, 278).

α-Chloro-ωα-di-bromo-propane $CH_3.CClBr.CH_2Br$. (170°). S.G. ^{0} 2·064 (Friedel, *A.* 112, 237). From $CH_3.CCl{:}CH_2$ and Br (F. a. S.; R.). With alcoholic KOH it gives C_3H_4ClBr and ethyl-propargyl oxide $CH{⋮}C.CH_2O.Et$ (Oppenheim, *A. Suppl.* 6, 372).

ω-Chloro-αβ-di-bromo-propane $CH_2Br.CHBr.CH_2Cl$. (195°) (O.); (203°) (R.). S.G. ^{0} 2·085 (R.). From allyl chloride and Br (O.). Also from epichlorhydrin



$\overset{O}{\overbrace{CH_2.CH}}.CH_2Cl$

and PBr_5 or PCl_3Br_2 (Reboul, *A. Suppl.* 1, 230; Darmstädter, *A.* 152, 320). Solid KOH gives $CH_2{:}CBr.CH_2Cl$. Alcoholic KOH gives rise to $CH{⋮}C.CH_2.OEt$.

α-Chloro-ωβ-di-bromo-propane $CH_2Br.CHCl.CH_2Br$. (200°). From glycerin dibromhydrin and PCl_5 (Berthelot a. de Luca, *J. pr.* 72, 317).

Chloro-tri-bromo-propane $C_3H_4ClBr_3$. (238°). S.G. ^{14} 2·39. From chloro-bromo-propylene (from glycide) and Br (Reboul, *A. Suppl.* 1, 231).

Di-chloro-bromo-propane $C_3H_5Cl_2Br$. (180°–187°). From allyl bromide and ClBr at 100° (M. Simpson, *Pr.* 27, 119).

ωβ-Di-chloro-α-bromo-propane $CH_2Cl.CHBr.CH_2Cl$. (176°). From *s*-dichlorhydrin and PBr_5 (Berthelot a. de Luca, *J. pr.* 17, 317).

ωα-Di-chloro-β-bromo-propane $CH_2Cl.CHCl.CH_2Br$. From $CH_2Cl.CH(OH).CH_2Br$ and PBr_5.

Di-chloro-bromo-propane $C_3H_5Cl_2Br$. (156°-160°). From bromo-propylene and chlorine (Linnemann, *A*. 138, 123).

ωα-**Di-chloro-*αβ*-di-bromo-propane** $CH_2Cl.CClBr.CH_2Br$. (205°). S.G. ^{0} 2·161. From $CH_2Cl.CCl{:}CH_2$ and Br (Friedel a. Silva, *C. R.* 74, 805; 75, 81; *Bl.* [2] 17, 386).

ωβ-**Di-chloro-*αβ*-di-bromo-propane** $CH_2Cl.CHBr.CHClBr$. (221°) (F. a. S.); (212°) (Hartenstein, *J. pr.* [2] 7, 313). S.G. ^{0} 2·19 (F. a. S.); $^{17\cdot5}$ 2·083 (H.). From $CH_2Cl.CH{:}CHCl$ and Br (R.; F. a. S.; H.).

ωα-**Di-chloro-*ωα*-di-bromo-propane** $CH_3.CClBr.CHClBr$. (189°). From allylene di-chloride and Br (F. a. S.; Pinner, *A*. 179, 44). Alcoholic KOH gives $C_3H_3Cl_2Br$ (143°).

Di-chloro-tri-bromo-propane $C_3H_3Cl_2Br_3$. [207°]. From di-chloro-bromo-propylene (143°) and Br (P.). Alcoholic KOH re-converts it into $C_3H_3Cl_2Br$.

β-CHLORO-α-BROMO-PROPIONIC ACID $CH_2Cl.CHBr.CO_2H$. [37°]. (c. 213°). Formed by the action of HNO_3 on the product of the union of BrOH with allyl chloride (Henry, *B*. 7, 757).

α-Chloro-β-bromo-propionic acid $CH_2Br.CHCl.CO_2H$. [37°]. (c. 213°). Formed similarly by oxidising the product of the union of ClOH with allyl bromide (H.).

Chloro-tri-bromo-propionic acid $C_2HClBr_3.CO_2H$. [103°]. From chloro-bromo-acrylic acid [70°] and Br (1 mol.) by heating for 2 hours at 100°; the yield is 70 p.c. (Mabery a. Weber, *Am.* 4, 104; 5, 255; *P. Am. A.* 17, 106). Triclinic prisms (from CS_2); v. sol alcohol and ether. Boiling baryta-water forms C_2HClBr_2; cold baryta-water gives chloro-di-bromo-acrylic acid.—KA′aq.—CaA′$_2$.—BaA′$_2$: S. 23 at 20°.

Di-chloro-di-bromo-propionic acid $C_2HCl_2Br_2.CO_2H$. [95°]. Prepared by the combination of di-chloro-acrylic acid [86°] by heating with bromine at 100° for several hours (Hill a. Mabery, *P. Am. A.* 17, 140; *Am.* 4, 267; *B.* 14, 1679). Triclinic prisms, $a{:}b{:}c = 1{\cdot}023{:}1{:}1{\cdot}052$; $\alpha = 91°$; $\beta = 76° 31'$; $\gamma = 108° 52'$. V. sol. water, alcohol, and ether, m. sol. CS_2 or benzene

Salts.—A′Ag: flat needles.—A′$_2$Ba: long easily soluble needles.

αβ-**Di-chloro-*ββ*-di-bromo-propionic acid** $CClBr_2.CHCl.CO_2H$. [100°]. Prepared by passing chlorine into di-bromo-acrylic acid at 100°; the yield is 96 p.c. (Mabery a. Nicholson, *Am.* 6, 166; *cf. Am.* 4, 270; *P. Am. A.* 17, 140; *B.* 14, 1680). Monoclinic prisms, v. e. sol. ether and alcohol, sol. hot $CHCl_3$ and CS_2, sl. sol. water.

Salts.—CaA′$_2$ 1½aq.—KA′2aq.

Tri-chloro-bromo-propionic acid $C_2HCl_3Br.CO_2H$. [84°]. Prepared by passing chlorine into a cold chloroform solution of chloro-bromo-acrylic acid in sunlight. The yield is 90 p.c. (Mabery, *Am.* 9, 1). Trimetric prisms; sl. sol. water, sol. ether, alcohol, and $CHCl_3$. Its salts are unstable.—KA′2aq: trimetric plates.—CaA′$_2$: oblique prisms.—BaA′$_2$: gummy.

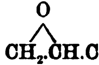
Tetra-chloro-bromo-propionic acid $CBrCl_2.CCl_2.CO_2H$. [225°]. Prepared by passing chlorine into a solution of bromo-propiolic acid in chloroform, till the product crystallises out (Mabery, *Am.* 6, 155). Sl. sol. CS_2 and chloroform. Its salts are unstable.

α-CHLORO-β-BROMO-PROPYL ALCOHOL C_3H_6ClBrO *i.e.* $CH_2Br.CHCl.CH_2OH$. (197°). S.G. ^{0} 1·764. From allyl bromide and HOCl (Henry, *B.* 7, 409, 758). Oxidation gives chloro-bromo-propionic acid (*v. supra*).

β-Chloro-α-bromo-propyl alcohol $CH_2Cl.CHBr.CH_2OH$. (197°). S.G. ^{11} 1·759. From allyl chloride and HOBr (H.). Oxidised by HNO_3 to chloro-bromo-propionic acid [37°], (215°).

Nitrate $CH_2(NO_3).CHBr.CH_2OH$. From the alcohol, HNO_3 and H_2SO_4. Oil.

α_1-chloro-α_2-bromo-isopropyl alcohol $CH_2Br.CH(OH).CH_2Cl$. *Chloro-bromhydrin.* (197°). S.G. ^{12} 1·740. From epichlorhydrin and HBr, or from epibromhydrin and HCl (Reboul, *A. Suppl.* 1, 225). Conc. KOH splits it up into HBr and epichlorhydrin. Oxidation gives chloro bromo-acetone [35°] (Theegarten, *B.* 6, 1212). Also from epichlorhydrin and Br at 100° (Grimaux a. Adam, *Bl.* [2] 33, 257).

Ethyl ether $C_3H_5ClBr.OEt$. (187°). From epichlorhydrin  $\overset{O}{\widehat{CH_2.CH}}.CH_2Cl$ and EtBr at 200° (Reboul a. Lourenço, *A.* 119, 238).

CHLORO-BROMO-PROPYL-BENZENE *v.* CHLORO-BROMO-CUMENE.

CHLORO-BROMO-PROPYLENE C_3H_4ClBr *i.e.* $CH_2{:}CCl.CH_2Br$. (121°). From α-chloro-allyl alcohol and PBr_3 (Henry, *C. R.* 95, 849).

Chloro-bromo-propylene $CHBr{:}CH.CH_2Cl$. (120°). S.G. ^{11} 1·63. From β-bromo-allyl alcohol and PCl_5 (Henry, *B.* 5, 453).

Chloro-bromo-propylene $CH_2{:}CBr.CH_2Cl$ (127°) (R.); (120°) (H.). S.G. ^{14} 1·69 (R.). From $CH_2Br.CHBr.CH_2Cl$ and solid KOH (Reboul, *A. Suppl.* 1, 230; Oppenheim, *A. Suppl.* 6, 374). From β-bromo-allyl alcohol and PCl_5 (H.).

Chloro-bromo-propylene $CH_3.CCl{:}CHBr$ (?) (105°). From $CH_3.CClBr.CH_2Br$ and alcoholic KOH (Friedel, *A.* 112, 237).

Di-chloro-bromo-propylene $CH_3.CCl{:}CClBr$(?) (143°). From allylene di-chloro-di-bromide and alcoholic KOH (Pinner, *A.* 179, 45). Br gives $C_3H_3Cl_2Br_3$ [207°].

CHLORO-BROMO-QUINONE $C_6H_2ClBrO_2$ [172°]. Formed by oxidation of chloro-bromo-hydroquinone (Schulz, *B.* 15, 656).

m-**Di-chloro-*m*-di-bromo-quinone** $C_6Cl_2Br_2O_2$ [6:2:5:3:4:1]. [233°].

Formation.—1. Formed by the action of Br on di-chloro-phenylene di-imide (from bleaching-powder and *p*-phenylene-diamine hydrochloride) (Krause, *B.* 12, 53).—2. By bromination of *m*-di-chloro-quinone $C_6H_2Cl_2O_2$ [6:2:4:1] (Levy, *B.* 16, 1447).—3. By bromination of *p*-di-chloro-quinone $C_6H_2Cl_2O_2$ [6:3:4:1] (Levy, *B.* 18, 2367); in this case one of the Cl atoms must undergo transposition from the *p* to the *m*-position.—4. From hydroquinone, conc. HCl and Br (Benedikt, *M.* 1, 347).

Properties.—Monoclinic golden-brown tables; $a{:}b{:}c = 1{\cdot}445{:}1{:}3{\cdot}0286$; $\beta = 74° 31'$ (L.). Sl. sol. ether and alcohol, insol. water.

Reactions.—It is very readily reduced by hydroxylamine hydrochloride to the corresponding hydroquinone [234°], whose acetyl derivative melts at [270°] (Hantzsch a. Schniter, *B.* 20, 2279) By boiling with aqueous alkalis it is converted into a chloro-bromo-di-oxy-quinone $C_6ClBr(OH)_2O_2$.

Tri-chloro-bromo-quinone $C_6Cl_3BrO_2$. From tri-chloro-quinone and Br at 130° (Stenhouse, *A. Suppl.* 6, 219). Also from tri-chloro-bromo-hydroquinone and conc. HNO_3 (Levy a. Schultz, *A.* 210, 162). Golden monoclinic pyramids; *a*:*b*:*c* 1·48:1:2·95; $\beta=74°\ 41'$. Sublimes at 160°. Dilute KOH gives chloro-bromo-di-oxy-quinone.

CHLORO-DI-BROMO-RESORCIN $C_6HBr_2Cl(OH)_2$. [105°]. Got by adding excess of bromine water to a solution of chloro-resorcin at 80°. Crystallises from water in silky needles (G. Reinhard, *J. pr.* [2] 17, 325).

Chloro-di-bromo-resorcin $C_6HBr_2Cl(OH)_2$. [86°]. From $C_6HBr_2Cl(OCl)(OBr)$ and $NaHSO_3$ (Benedikt, *M.* 4, 227).

Di-chloro-bromo-resorcin $C_6HBrCl_2(OH)_2$. [100°]. From Br and di-chloro-resorcin. Silky needles (from water) (R.).

Di-chloro-tri-bromo-resorcin $C_6HCl_2Br_3O_2$ *i.e.* $C_6HBr_2Cl(OCl)(OBr)$(?) Formed by adding Br (216 g.) dissolved in conc. HClAq (1,000 c. c.) to a solution of resorcin (50 g.) in water (2,000 c. c.) (B.). Yellow crystals. At 175° it gives crystalline $C_{12}H_4Cl_4Br_2O_4$ which is reduced by tin and HCl to di-chloro-di-bromo-tetra-oxy-diphenyl.

Tri-chloro-di-bromo-resorcin $C_6HCl_3(OBr)_2$. [100°]. Prepared by adding Br to tri-chloro-resorcin suspended in dilute HCl (B.). Small golden crystals. Gives off Br (1 mol.) on heating. Reduced by tin and HCl to tri-chloro-resorcin.

HEXA-BROMO-TRI-CHLORO-DI-THIENYL-ETHANE $CCl_3.CH(C_4Br_3S)_2$. [176°]. Formed by bromination of di-thienyl-tri-chloro-ethane (Peter, *B.* 17, 1343). White crystalline powder. V. sol. ether and chloroform, sl. sol. alcohol. Does not give the indophenine reaction.

CHLORO-BROMO-THYMOQUINONE $C_6MePrClBrO_2$ [1:4:5:2:3:6]. [78°]. Formed by bromination of *m*-chloro-thymoquinone $C_6HMePrClO_2$[1:4:5:3:6]. Yellow plates (Schniter, *B.* 20, 1319).

Chloro-bromo-thymoquinone $C_6MePrClBrO_2$ [1:4:2:5:3:6]. *p-Chloro-benzyl bromide.* [87°]. *Formation.*—1. By oxidation of the corresponding hydroquinone with Fe_2Cl_6.—2. By bromination of *o*-chloro-thymo-quinone $C_6HMePrClO_2$[1:4:2:3:6]. Golden-yellow plates (Schniter, *B.* 20, 1318).

***p*-CHLORO-ω-BROMO-TOLUENE** C_7H_6ClBr *i.e.* $C_6H_4Cl.CH_2Br$. [48·5°] (225°–230°). From *p*-chloro-toluene and Br (Jackson a. Field, *Am.* 1, 102). White needles (from alcohol); aromatic odour; volatile in the air.

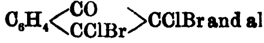
ω-Chloro-*p*-bromo-toluene $C_6H_4Br.CH_2Cl$. *b-Bromo-benzyl chloride.* Obtained, mixed with an equivalent quantity of $C_6H_4Br.CH_2Br$, by brominating benzyl chloride (Errera, *G.* 17, 193). NaOEt converts it into $C_6H_4Br.CH_2.OEt$ (243°).

Di-chloro-bromo-toluene $C_7H_5Cl_2Br$. (280°–290°) (Jackson a. Field, *B.* 11, 905).

CHLORO-BROMO-TOLUQUINONE $C_6HMeClBrO_2$. [111°]. From the hydroquinone [123°], by oxidation. Thick needles. V. sol. ether, benzene, and chloroform; scarcely sol. water (Schniter, *B.* 20. 2287).

Chloro-bromo-toluquinone $C_6HMeClBrO_2$. [150°]. From the hydroquinone, [121°], by oxidation. Glistening yellow plates (from alcohol) (Schniter, *B.* 20, 2287).

TRI-CHLORO-DI-BROMO-DI-TOLYL-ETHANE $C_{16}H_{13}Cl_3Br_2$. [148°]. From tri-chloro-di-tolyl-ethane and Br in CS_2 (O. Fischer, *B.* 7, 1191).

DI-CHLORO-BROMO-VINYL-BENZOIC ACID $C_9H_5Cl_2BrO_2$ *i.e.* $CClBr:CCl.C_6H_4.CO_2H$. [174°]. From  $C_6H_4{<}{\substack{CO \\ CClBr}}{>}CClBr$ and alcoholic NaOH diluted with water (Zincke a. Fröhlich, *B.* 20, 2056). Needles.

Methyl ether MeA′. [82°].

CHLORO-BUTANE *v.* BUTYL CHLORIDE.

αα-Di-chloro-butane $CH_3.CCl_2.CH_2.CH_3$. (96°). From methyl ethyl ketone and PCl_5 (Bruylants, *B.* 8, 412). Dry KOH gives $CH:C.CH_2.CH_3$. Alcoholic KOH gives $CH_3.C:C.CH_3$ (Favorsky, *Bl.* [2] 45, 247).

ωω-Di-chloro-isobutane $(CH_3)_2CH.CHCl_2$. *Isobutylidene chloride.* (104°). S.G. $\underline{12}$ 1·011. V.D. 127 (H = 1). From isobutyric aldehyde and PCl_5 (Oeconomides, *C. R.* 92, 884). Aqueous NH_3 at 180° gives chloro-isobutylene (67°).

Di-chloro-isobutane $C_4H_8Cl_2$. (107°). From chloro-isobutylene $CH_2:CMe.CH_2Cl$ and conc. HCl (Chéchoukoff, *Bl.* [2] 43, 112).

Di-chloro-butane $C_4H_8Cl_2$. (128°) (P.); (125°) (Faraday). S.G. $\underline{28}$ 1·112. V.D. 4·43. Formed by union of Cl with the mixture of butylenes (*q. v.*) obtained by treating isobutyl alcohol (25 pts.) with H_2SO_4 (25 pts.), $CaSO_4$ (40 pts.), and K_2SO_4 (10 pts.) (Puchot, *A. Ch.* [5] 28, 508; *cf.* Faraday, *Tr.* 1825, 440; Kolbe, *A.* 69, 269; 64, 339).

Di-chloro-butane $C_4H_8Cl_2$. (106°). From *tert*-butyl chloride and Cl in daylight (D'Ottreppe de Bouvette, *Belg. Acad. Bull.* [3] 4, 359).

Tetra-chloro-butane $C_4H_6Cl_4$ *i.e.* $CH_3.CCl_2.CHCl.CH_2Cl$. (85°) at 10 mm. From tri-chloro-butyl alcohol by gradual addition of PCl_5 (Garzarolli-Thurnlackh, *A.* 213, 372). Oil.

Tetra-chloro-butane $CH_2Cl.CHCl.CHCl.CH_2Cl$. *Butinene tetra-chloride.* [73°]. From butinene and Cl. Also from erythrite and PCl_5 (Henninger, *Bl.* [2] 34, 195). Prisms.

Tetra-chloro-iso-butane $CCl_3.CMe_2Cl$. *Tri-chloro-tri-methyl-carbinyl chloride* or *chloro-isobutyro-tri-chloride.* (167°). Strong odour. Formed, together with hexa-chloro-di-*tert*-butyl oxide $(CCl_3.CMe_2)_2O$, by the action of PCl_5 upon acetone-chloroform (Willgerodt a. Dürr, *B.* 20, 539).

Hexa-chloro-butane $C_4H_4Cl_6$. (148°) at 50 mm. S.G. $\underline{12}$ 1·67. A liquid formed by the action of chlorine on isobutyl iodide (Prunier, *Bl.* [2] 24, 24).

Hexa-chloro-butane $C_4H_4Cl_6$. Formed by the action of chlorine on $C_4H_8Cl_2$ (from isobutyl alcohol) in sunlight (Puchot, *C. R.* 85, 757). Oil. Converted by KOH into $C_4H_2Cl_4$, C_4Cl_2, and C_4Cl_4.

Hexa-chloro-butane $C_4H_4Cl_6$. (c. 115°) *in vacuo.* From *tert*-butyl chloride and chlorine in sunlight (d'O. de B.).

Hepta-chloro-butane $C_4H_3Cl_7$. [36°]. (125°–135°) *in vacuo.* From *tert*-butyl chloride and Cl in sunlight (d'O. de B.).

Hepta-chloro-butane $C_4H_3Cl_7$. [42°]. (135°–145°) *in vacuo*. Formed at the same time as the preceding.

CHLORO-BUTANE TETRA-CARBOXYLIC ACID $CCl(CO_2H)_2.C(C_2H_5)(CO_2H)_2$. *Ethyl-chloro-acetylene-tetra-carboxylic acid.*

Tetra-ethyl-ether $A^{iv}Et_4$. S.G. $\frac{20}{15}$ 1·076. Formed by chlorination of butane-tetra-carboxylic ether. Oil (Bischoff a. Rach, *B.* 17, 2786).

CHLORO-BUTENYL ALCOHOL C_4H_7ClO. *Chloro-crotyl alcohol.* (158·3° i.V.) at 742·5 mm. S.G. $\frac{15.8}{15.8}$ 1·1312. V.D. 3·60 (for 3·68). From tri-chloro-butyl alcohol by zinc-dust and HCl (Garzarolli-Thurnlackh, *A.* 213, 375). Crystallises in a freezing mixture. Smells like allyl compounds. M. sol. water, but separated by K_2CO_3 or NaCl. Forms with Br in $CHCl_3$ chloro-di-bromo-butyl alcohol, which is very unstable. If it be oxidised by HNO_3 it forms chloro-di-bromo-butyric acid (not isolated), which is reduced by zinc-dust and HCl to chloro-crotonic acid [97°].

Acetate (168°–169°) at 741 mm. V.D. 5·23 (for 5·14). Colourless fruity liquid, heavier than water. V. sl. sol. water.

CHLORO-BUTINENE C_4H_5Cl. (65°). From di-chloro-butylene $CH_3.CH:CH.CHCl_2$ and alcoholic KOH (Kekulé, *A.* 162, 99).

Hexa-chloro-butinene C_4Cl_6. [39°]. (284°). From *s*-hexyl-iodide and ICl_3 at 100°–240° (Krafft, *B.* 10, 803). Thin prisms (from alcohol).

TRI-CHLORO-BUTYL ACETATE $C_4H_6Cl_3OAc$. (217·5°) at 733 mm. S.G. $\frac{8.5}{8.5}$ 1·344. From tri-chloro-butyl alcohol and AcCl at 110° (Garzarolli-Thurnlackh, *A.* 213, 373).

***a*-CHLORO-ISOBUTYL ALCOHOL** C_4H_9ClO *i.e.* $(CH_3)_2CCl.CH_2OH$ *Butylene-glycol chlorhydrin* (137°). From isobutylene and HClO (Butlerow, *A.* 144, 25). Sl. sol. water. Reduced by sodium-amalgam to isobutyl alcohol. Oxidised by HNO_3 to chloro-isobutyric acid (Henry, *B.* 9, 1034).

Chloro-*sec*-butyl alcohol. *Ethyl ether* $CH_3.CH_2.CH(OEt).CH_2Cl$. (141°). S.G. ^{0} ·9735. From di-chloro-di-ethyl oxide and $ZnEt_2$ (Lieben, *A.* 123, 133).

Di-chloro-*tert*-butyl alcohol $C_4H_8Cl_2O$. (143·5° i.V.). S.G. ^{0} 1·0335. From $(CH_3)_2C:CHCl$ and HClO (Oeconomides, *C. R.* 92, 1235).

Tri-chloro-butyl alcohol $CH_3.CCl_2.CHCl.CH_2.OH$ [62°]. (120°) at 45 mm. From tri-chloro-butyric aldehyde (butyl chloral) and $ZnEt_2$, $ZnPr_2$, or $Zn(CH_2Pr)_2$, followed by water, thus: $C_3H_4Cl_3CHO + Zn(C_2H_5)_2 = C_3H_4Cl_3.CH_2OZnC_2H_5 + C_2H_4$ (Garzarolli-Thurnlackh, *A.* 213, 370; 223, 166). Also from urochloralic acid and HCl (Mering, *H.* 4, 93). Prisms (from ether). V. sol. alcohol or ether, sl. sol. hot water. Sol. warm conc. H_2SO_4, but decomposed by heating the solution.

Reactions.—1. PCl_3 has hardly any action. 2. Fuming HBr at 110° has no action.—3. PCl_5 gives tetra-chloro-butane.—4. Fuming HNO_3 gives tri-chloro-butyric acid.—5. *Zinc-dust* and HCl reduce it to chloro-butenyl alcohol (*q.v.*).

Tri-chloro-*tert*-butyl-alcohol *v.* ACETONE-CHLOROFORM

CHLORO-ISO-BUTYL- SO-AMYL-GLYOXALINE (?) $C_{12}H_{21}ClN_2$. *Chloro-oxalamyline.* (267°–270°). Prepared from di-isoamyl-oxamide in the same way as chloro-oxalethyline from di-ethyl-oxamide (Wallach a. Schulze, *B.* 13, 516; *A.* 214, 316).

Salts.—$(B'HCl)_2PtCl_4$.—B'HCl.

γ-CHLORO-*n*-BUTYL-BENZENE $C_{10}H_{13}Cl$ *i.e* $C_6H_5.CHCl.C_3H_7$. From $C_6H_5.CH(OH).C_3H_7$ and HCl (Engler a. Bethge, *B.* 7, 1128). Liquid.

CHLORO-ISO-BUTYLENE $(CH_3)_2C:CHCl$. *Iso-butenyl chloride. Isocrotyl chloride.* (c. 65°). S.G. ^{12} ·979. V.D. 89·7. From isobutylidene chloride $(CH_3)_2CH.CHCl_2$ and alcoholic KOH or NH_3. Formed together with $(CH_3)_2CH.CHCl_2$, by treating isobutyric aldehyde with PCl_5 (Oeconomides, *C. R.* 92, 884, 1235; *Bl.* [2] 35, 498). Formed also by the action of chlorine on isobutylene, especially below 0° (Scheschukoff, *J. R.* 16, 493; *Bl.* [2] 41, 253; 43, 127). Converted by water at 90° into isobutyric aldehyde.

Chloro-isobutylene $CH_3.C(CH_2Cl):CH_2$. *Butenyl chloride.* (c. 73°). S.G. ^{0} ·955. Formed, together with the preceding, by chlorinating isobutylene, especially above 0° (S.). Heated with aqueous K_2CO_3 it forms isobutenyl alcohol (113°). HCl forms $C_4H_8Cl_2$ (107°), whence K_2CO_3 gives $C_4H_8(OH)_2$ (178°).

Di-chloro-*n*-butylene $CH_3.CH:CH.CHCl_2$. (126°). S.G. ^{20} 1·131. From crotonic aldehyde and PCl_5 (Kekulé, *A.* 162, 98) Alcoholic KOH gives C_4H_5Cl (65°) and $C_4H_6Cl.OEt$ (134). Br gives $C_4H_6Cl_2Br_2$ whence aqueous K_2CO_3 gives $C_4H_6ClBr(OH)_2$ (c. 118°).

Tetra-chloro-butylene $C_4H_4Cl_4$. (200°). From tri-chloro-butyric aldehyde and PCl_5 (Judson, *B.* 3, 790).

Penta-chloro-butylene $C_4H_3Cl_5$. (187°) at 460 mm. From *tert*-butyl alcohol and chlorine (Lieben, *B.* 8, 1017).

TRI-CHLOR-BUTYLIDENE-IMIDE $CH_3.CHCl.CCl_2.CH:NH$. [164°–165°]. (P. a. K.); [170°] (S.). Prepared by the action of ammonium acetate on tri-chloro-butyric ortho-aldehyde (hydrate of butyrochloral) (Pinner a. Klein, *B.* 11, 1491). Also by heating tri-chloro-butyric aldehyde-ammonia with benzoic aldehyde (R. Schiff, *G.* 9, 438). Sol. alcohol, ether, hot water and hot benzene.

***a*-CHLORO-ISOBUTYL-MALONIC ACID** $C_4H_9.CCl:(CO_2H)_2$. *Di-ethyl-ether* $A''Et_2$. (246°). S.G. ^{15} 1·091. Prepared by the action of chlorine on isobutyl-malonic ether. Liquid. On saponification with KOH it gives iso-butyl-oxy-malonic acid (Conrad a. Bischoff, *B.* 13, 600; *A.* 209, 237).

HEXA-CHLORO-DI-TERT-BUTYL OXIDE $C_8H_{12}Cl_6O$ *i.e.* $(CCl_3.CMe_2)_2O$. '*Acetone-chloroform ether.*' (156°). Formed, together with $CCl_3.CMe_2OH$, and its oily isomeride, by the action of PCl_5 upon acetone-chloroform (Willgerodt a. Dürr, *B.* 20, 539). Liquid. Volatile with steam. Very pungent.

***a*-CHLORO-*n*-BUTYRIC ACID** $C_4H_7ClO_2$ *i.e.* $CH_3.CH_2.CHCl.CO_2H$. From its chloride and water. Thick liquid, v. sol. hot water.

Chloride $CH_3.CH_2.CHCl.COCl$. (c. 131°). S.G. ^{17} 1·257. Formed by chlorinating butyryl chloride in presence of iodine (Markownikoff, *A.* 153, 241; *cf.* *Z.* [2] 4, 621).

Ethyl ether EtA'. (c. 158°). S.G. $^{17\cdot5}$ 1·063 (M.).

β-Chloro-*n*-butyric acid $CH_3.CHCl.CH_2.CO_2H$.

Formation.—1. By saponification of allyl cyanide by HCl (Pinner, *B.* 12, 2056).—2. By oxidation of the corresponding aldehyde (Karetnikoff, *J. R.* 11, 252).—3. By treating the hydrochloride of β-chloro-butyric imido-ether $CH_3.CHCl.CH_2.C(NH)(OEt)$ with water (Pinner, *B.* 17, 2008).

Reactions.—Boiling baryta-water forms HCl and crotonic acid.

Ethyl ether EtA'. (c. 170°). S.G. ^{0} 1·072 (Ba.); $\frac{20}{4}$ 1·0517 (Br.). μ_β 1·430. R_∞ 59·1. Obtained by chlorinating butyric acid (Balbiano, *B.* 10, 1749; 11, 348; *G.* 10, 137). Probably the same compound is got by saturating an alcoholic solution of crotonic acid with HCl (Bruhl, *A.* 203, 28). Converted by KOH into crotonic acid and β-oxy-butyric acid. Heated with alcoholic NH_3 it gives β-amido-butyramide.

γ-Chloro-butyric acid $CH_2Cl.CH_2.CH_2.CO_2H$. [10°]. S.G. $\frac{10}{}$ 1·250. From the nitrile by HCl (Henry, *C. R.* 101, 1158). Viscous liquid or thin laminæ, sl. sol. water. At 190° it splits up into HCl and the lactone of γ-oxy-butyric acid.

Methyl ether MeA'. (174°). S.G. $\frac{10}{10}$ 1·894. From the nitrile, MeOH, and HCl.

Ethyl ether EtA'. (184°). S.G. $\frac{10}{10}$ 1·122.

Chloride $CH_2Cl.CH_2.CH_2.COCl$. (174°). S.G. $\frac{10}{10}$ 1·268.

Amide $CH_2Cl.CH_2.CH_2.CONH_2$. [90°].

Nitrile $CH_2Cl.CH_2.CH_2.CN$. (196°). S.G. $\frac{10}{10}$ 1·162. From $CH_2Cl.CH_2.CH_2Br$ and KCy.

α-Chloro-isobutyric acid $(CH_3)_2CCl.CO_2H$. From $(CH_3)_2CCl.CH_2OH$ by oxidation with HNO_3 (Henry, *Bl.* [2] 26, 24). Formed also by chlorinating isobutyric acid (Balbiano, *B.* 11, 1693).

Ethyl ether EtA'. (149° cor.). S.G. ^{0} 1·062. Converted by alkalis into oxy-isobutyric, methacrylic, and 'di-butyllactic' ($C_8H_{14}O_5$) acids (Testa, *G.* 10, 377).

αβ-Di-chloro-butyric acid $CH_3.CHCl.CHCl.CO_2H$ [63°]. Formed by combining solid crotonic acid with chlorine, in CS_2 solution. Large glistening colourless prisms. By aqueous NaOH at the ordinary temperature it is converted into *allo*-α-chloro-crotonic acid [66°]. If the solution is heated during the reaction some ordinary α-chloro-crotonic acid is formed simultaneously. On heating the neutral alkaline salts in aqueous solution *allo*-α-chloro-propylene is formed (Wislicenus, *B.* 20, 1008; Michael a. Brown, *Am.* 9, 281; *J. pr.* [2] 36, 174; *cf.* Friedrich, *A.* 219, 371).

Salts.—AgA'.—BaA'$_2$: gummy.

Methyl ether MeA'. (84°) at 28 mm.; (177°). S.G. $\frac{0}{4}$ 1·2809 (Zeisel, *M.* 7, 368).

Ethyl ether EtA'. (96°) at 35 mm. Converted by alcoholic KOH into α-chloro-crotonic acid [98°].

Chloride $CH_3.CHCl.CHCl.COCl$. (164°). From crotonic aldehyde and chlorine (Z.).

***Allo*-αβ-di-chloro-butyric acid** $CH_3.CHCl.CHCl.CO_2H$. Liquid. Formed, together with some solid αβ-di-chloro-butyric acid [63°], by combination of liquid iso-crotonic acid with Cl. By excess of cold aqueous NaOH it is converted into ordinary α-chloro-crotonic acid [99°]. On heating the neutral aqueous solution of the alkaline salts, ordinary α-chloro-propylene (36°) is formed (Wislicenus, *B.* 20, 1009).

A di-chloro-butyric acid is formed by chlorinating *n*-butyric acid in sunlight (Pelouze a. Gélis, *A. Ch.* [3] 10, 434; Naumann, *A.* 119, 120).

αα-Di-chloro-butyric acid. *Anilide.* $CH_3.CH_2.CCl_2.O.NHPh$. [200°]. From aniline ethyl-malonate and PCl_5 (Schramm, *B.* 21, 289). Distillation with aqueous Na_2CO_3 converts it into NPh:CH.O.CClEt.CO NHPh which yields phenyl-carbamine when boiled with conc. KOHAq.

o-Toluide $CH_3.CH_2.CCl_2.ONHC_7H_7$. Prepared in a similar way. Is converted by aqueous Na_2CO_3 into $NC_7H_7{:}CH.O.CClEt.CO.NHC_7H_7$. [107°].

Tri-chloro-butyric acid $CH_3.CHCl.CCl_2.CO_2H$. [60°] (K.); [58°] (G.). (237°). S. 4. Formed by oxidising tri-chloro-butyric aldehyde (Krämer a. Pinner, *B.* 3, 389; Judson, *B.* 3, 785; Kahlbaum, *B.* 12, 2337). From the alcohol and fuming HNO_3 (Garzarolli-Thurnlackh, *A.* 213, 374; 182, 185). The silver salt when boiled with water gives di-chloro-propylene (78°).—AgA'.—CaA'$_2$.—PbA'$_2$.

Ethyl ether EtA'. (212°).

Chloride $CH_3.CHCl.CCl_2.COCl$. (c. 164°).

Amide $CH_3.CHCl.CH_2.CONH_2$. [96°].

Tri-chloro-butyric acid $CH_2Cl.CH_2.CCl_2.CO_2H$. [75°]. S. 5. From the corresponding aldehyde and fuming HNO_3 (Natterer, *M.* 4, 539; 5, 251).

Tri-chloro-isobutyric acid $C_4H_5Cl_3O_2$. [50°]. Separates when chlorine is passed into an aqueous solution of sodium citraconate (Gottlieb, *J. pr.* [2] 12, 1). Prisms. Boiling alkalis convert it into di-chloro-methacrylic acid. Zinc-dust and HCl form chloro-methacrylic acid.

Salts.—NH$_4$A'.—BaA'$_2$.—PbA'$_2$.—Aniline salt NH$_2$PhHA'. [164°] (Daccomo, *J.* 1884, 1385).—[4:1]$C_6H_4Me.NH_3A'$. [154°] (D.).

Tetra-chloro-butyric acid $C_4H_4Cl_4O_2$. [140°]. From *n*-butyric acid and Cl in sunlight (Pelouze a. Gélis, *A. Ch.* [3] 10, 434).

β-CHLORO-*n*-BUTYRIC ALDEHYDE C_4H_7ClO *i.e.* $CH_3.CHCl.CH_2CHO$. [97°]. From crotonic aldehyde and gaseous HCl (Kekulé, *A.* 162, 100). Needles (from dilute alcohol); insol. water.

Tri-chloro-butyric aldehyde $CH_3.CHCl.CCl_2.CHO$.

Butyl-chloral. Mol. w. 175½. (165°). S.G. $\frac{20}{4}$ 1·3956. μ_β 1·482. R_∞ 57·99 (Bruhl, *A.* 203, 20).

Formation.—1. By the action of chlorine on aldehyde (Pinner, *A.* 179, 21; *B.* 3, 383; 8, 1561). 2. From chloro-acetic ortho-aldehyde by heating with an equivalent quantity of aldehyde and a trace of HCl; the oily product (α-chloro-crotonic aldehyde) being subsequently chlorinated (Lieben a. Zeisel, *M.* 4, 531).

Properties.—Liquid; combines with water forming a crystalline hydrate, whence it is liberated by distillation in a current of HCl. Oxidation gives tri-chloro-butyric acid. PCl_5 gives $C_4H_4Cl_4$ (200°).

Reactions.—1. $ZnMe_2$ in ether followed, after a time, by water gives tri-chloro-amyl alcohol $(C_3H_4Cl_3)CHMeOH$.—2. $ZnEt_2$ (1 mol.) gives off ethylene, and the residue when treated with water forms tri-chloro-butyl alcohol (Garzarolli-Thurnlackh, *A.* 213, 370).—3. Tri-chloro-lactic acid at 130° gives $CCl_3.CH<\substack{O \\ CO_2}>CH.C_3H_4Cl_3$ [107°] (Wallach, *A.* 193, 47).—4. Lactic acid gives $CH_3.CH<\substack{O \\ CO_2}>CH.C_3H_4Cl_3$ (261°). — 5. Tri-chloro-oxy-valeric acid at 175° slowly forms $C_3Cl_3H_4CH<\substack{O \\ CO_2}>CH.C_3Cl_3H_4$ [85°]. (300°-310°) (W.).—6. PH_4I forms $C_8H_{14}Cl_6PO_2$ [96°] (Girard, *A. Ch* [6] 2, 52). Split up by conc. NaOHAq into HCl, H_3PO_3, $C_2H_4Cl_2$, formic acid and hydrogen.

Combinations. - 1. **With water**:— ***Tri-chloro-butyric ortho-aldehyde*** $CH_3.CHCl.CCl_2.CH(OH)_2$. Mol. w. 193½. [78°] (K. a. P.); [75°] (L. a. Z.). V.D. 3·33 (calc. 6·7) (Moitesier, *C. R.* 90, 1075). Trimetric laminæ; $a:b:c = \cdot65:1:1\cdot2$. Dissociated by heat. *Reactions.* - (*a*) Converted by boiling Na_2CO_3Aq into di-chloro-propylene (77°) which on oxidation with CrO_3 yields acetic acid.—(*b*) Zn and HCl reduce it to chloro-crotonic and crotonic aldehydes (Sarnow, *A.* 164, 108).—(*c*) Iron and HOAc give butyric aldehyde, *n*-butyric alcohol, and butenyl alcohol (Lieben a. Zeisel, *M.* 1, 840).

(*d*) After being taken into the system it is excreted in urine as **tri-chloro-butyl-glycuronic** acid $C_{10}H_{15}Cl_3O_7$ (Mering, *H.* 6, 491; Külz, *J. Th.* 1882, 95) This acid crystallises in silky needles, is lævorotatory, and split up by boiling dilute acids into glycuronic acid and tri-chloro-butyl alcohol.—(*e*) Heated with dry NH_4OAc it forms $C_4H_5Cl_3NH$ [165°] (Pinner a. Klein, *B.* 11, 1491); [170°] (Schiff, *B.* 11, 2167).

2. **With hydrogen cyanide**:— ***Tri-chloro-oxy-valeronitrile*** $CH_3.CHCl.CCl_2.CH(OH).CN$. [102°]. (c. 230°). This is converted by alcoholic NH_3 into chloro-crotonamide; and by H_2SO_4 into tri-chloro-oxy-valeramide. Heated with urea it yields chloro-crotonyl-urea $CH_3CH.CCl.CO.NH.CO.NH_2$ as chief product (about 60 p.c.) and **butyrochloral-biuret** $CH_3.CHCl.CCl_2.CH<\substack{NH.CO \\ NH\,CO}>NH$ as a by-product (about 6 p.c.) (Pinner a. Lifschütz, *B.* 20, 2347).

3. **With acetamide**:—$C_4H_5Cl_3(OH)(NHAc)$. [170°] (Pinner, *A.* 179, 40); [158°] (Schiff a. Tassinari, *B.* 10, 1785). Tables; v. sl. sol. water.

4. **With benzamide**:—$C_4H_5Cl_3(OH)(NHBz)$. [150°] (Pinner, *A.* 179, 40); [133°] (Schiff a. Tassinari, *B.* 10, 1785). Formed by melting tri-chloro-butyric aldehyde with benzamide.

5. **With carbamic ether**:— $C_4H_5Cl_3(OH)(NH.CO_2Et)$. [125°]. From tri-chloro-butyric aldehyde, carbamic ether, and HCl (Bischoff, *B.* 7, 632). Small prisms.

6. **With ammonia**:—[62°] (S. a. T.).

7. **With alcohol**:— $CH_3.CHCl.CCl_2.CH(OH)(OEt)$. Oil (P.).

8. **With acetyl chloride**:— $CH_3.CHCl.CH_2.CH(OAc)Cl$ (220°).

Tri-chloro-butyric aldehyde $CH_2Cl.CH_2.CCl_2.CHO$. [-78°]. From $\alpha\gamma$-di-chloro-crotonic aldehyde $CH_2Cl.CH:CCl.CHO$ and HCl (Natterer, *M.* 4, 551; 5, 253). Forms no hydrate.

β-CHLORO-BUTYRIMIDO-ETHYL-ETHER $C_3H_6Cl.C(NH).OEt$. The hydrochloride is formed by passing HCl into a mixture of alkyl cyanide (1 mol.) and ethyl alcohol (1 mol.). The hydrochloride (B'HCl) crystallises in large colourless prisms (Pinner, *B.* 17, 2007).

CHLORO-CAFFEINE *v.* CAFFEINE.

CHLORO-CAMPHOR *v.* CAMPHOR.

CHLORO-CAPROIC ACID *v.* CHLORO-HEXOIC ACID.

CHLORO-TRICARBALLYLIC ACID. ***Methyl ether*** $CH_2(CO_2Me).CCl(CO_2Me).CH_2(CO_2Me)$. From tri-methyl citrate and PCl_5 (Hunæus, *B.* 9, 1750). Oil; split up by heat into HCl and tri-methyl aconitate.

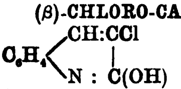
TRI-CHLORO-CARBAZOLE $C_{12}H_6Cl_3N$. [180°]. Prepared by passing chlorine into acetic acid containing carbazole in suspension until the mass appears bright green (Graebe, *A.* 202, 27). Needles; sol. benzene, ether, and alcohol. Its solution in conc. H_2SO_4 is bright green. Its **picric acid compound** [100°] forms red needles.

Hexa-chloro-carbazole $C_{12}H_3Cl_6N$. [225°]. Obtained by further chlorination of the above. Long needles; its solution in conc. H_2SO_4 is yellowish-green.

Octo-chloro-carbazole $C_{12}HCl_8N$. [275°]. Formed by chlorinating the above in presence of $SbCl_5$. Long needles, sl. sol. alcohol. Further chlorination in presence of $SbCl_5$ at 160° gives hexa-chloro-benzene.

CHLORO-CARBONIC ETHER *v.* CHLORO-FORMIC ETHER.

(β)-CHLORO-CARBOSTYRIL C_9H_6ClNO *i.e.*



$C_6H_4<\substack{CH:CCl \\ | \\ N:C(OH)}$

(*Py.* 2, 3)-*Chloro-oxy-quinoline.* [242°]. Formed by heating di-chloro-quinoline [104°] with dilute HCl to 120°. By PCl_5 it is converted back into the dichloro-quinoline [104°] (Friedländer a. Weinberg, *B.* 15, 336, 2679).

Ethyl ether $C_9H_5ClN(OEt)$: liquid, volatile with steam.

Chloro-carbostyril C_9H_6NOCl. [246°]. Formed by boiling a dilute HCl solution of *o*-amido-phenyl-propiolic acid (Baeyer a. Bloem, *B.* 15, 2148). Sublimable. Silky needles. Sl. sol. hot, insol. cold, water. May be identical with the above.

Di-chloro-carbostyril $C_9H_5Cl_2NO$. [249°]. Formed by chlorination of carbostyril (Friedländer a. Weinberg, *B.* 15, 1425). Fine white needles. PCl_5 converts it into tri-chloro-quinoline [161°].

DODECA-CHLORO-CEROTIC ACID $C_{27}H_{42}Cl_{12}O_2$. From cerotic acid and chlorine (Brodie, *A.* 67, 190). Gummy mass. EtA'.

CHLORO-CETYL ALCOHOL $C_{16}H_{33}ClO$. (300°). From cetene $C_{16}H_{32}$ and cold dilute HClO (Carius, *A.* 126, 195). Liquid. KOH gives $C_{16}H_{32}O$ [30°] (300°).

DI-CHLORO-CHELIDAMIC ACID *v.* CHELIDONIC ACID.

HEPTA-CHLORO-CHOLESTERIN *v.* CHOLESTERIN.

CHLORO-CHROMIC ACID. Name sometimes given to CrO_2Cl_2, *v.* CHROMIUM, *Oxychlorides of.*

CHLORO-CHRYSENE *v.* CHRYSENE.

α-CHLORO-CINNAMIC ACID

$C_6H_5.CH:CCl.CO_2H$. α *Chloro-β-phenyl-acrylic acid.* [142°].

Formation.—1. By heating sodium chloro-acetate with acetic anhydride and benzoic aldehyde (Plöchl, *B.* 15, 1945).—2. By heating α-chloro-β-oxy-β-phenyl-propionic acid with NaOAc and Ac_2O (Forrer, *B.* 16, 854).—3. Together with a small quantity of the β isomeride by heating $C_6H_5.CHCl.CHCl.CO_2H$ with alcoholic KOH (Jutz, *B.* **15**, 788).—4. By digesting benzoyl-acetic ether with PCl_5 and $POCl_3$ at 100° (Perkin, *C. J.* 47, 240). In this reaction the β acid might have been anticipated. Needles. Volatile with steam. V. sl. sol. water, v. sol. alcohol and ether, sl. sol. ligroïn.

β-Chloro-cinnamic acid $C_6H_5.CCl:CH.CO_2H$. ? *Allo-α-chloro-cinnamic acid.* [114°]. Formed as above (*Formation* 3) and separated from the α-acid by the smaller solubility of its potassium salt in alcohol. Trimetric crystals (Haushofer, *Z. K.* 8, 382, 389).

o-**Chloro-cinnamic acid** [2:1]$C_6H_4Cl.CH:CH.CO_2H$. [200°]. (G. a. H.); [196°] (S.). Formed by boiling *o*-diazo-cinnamic acid with strong HCl (Gabriel a. Herzberg, *B.* 16, 2036). Also by heating *o*-chloro-benzylidene-malonic acid to its melting-point (Stuart, *C. J.* 53, 141). Sol. alcohol, ether, and acetic acid, nearly insol. petroleum-ether and hot water.

m-**Chloro-cinnamic acid** [3:1]$C_6H_4Cl.C_2H_2.CO_2H$. [167°]. Formed by boiling *m*-diazo-cinnamic acid with strong HCl (G. a. H. *B.* 16, 2038). Needles. V. sol. hot water, hot alcohol and ether, sl. sol. benzene and petroleum-ether.

p-**Chloro-cinnamic acid** [4:1]$C_6H_4Cl.C_2H_2.CO_2H$. [242°]. Formed by boiling *p*-diazo-cinnamic acid with strong HCl (Gabriel a. Herzberg, *B.* 16, 2039). V. sol. alcohol, sl. sol. cold water, benzene, and ether.

Di-chloro-cinnamic acid $C_6H_3.Cl_2.CH:CHCO_2H$ [1:3:6]. Formed by the action of Ac_2O and NaOAc on (β)-dichloro-benzoic aldehyde (Seelig, *A.* 237, 168). Fine needles (from dilute alcohol).

(α)-Tri-chloro-cinnamic acid $C_6H_2Cl_3.CH:CH.CO_2H$ [1 3:4:6]. [201°]. Formed by acting on (α)-trichloro-benzoic aldehyde with acetic anhydride and sodium acetate (Seelig, *A.* 237, 151).

(β)-Tri-chloro-cinnamic acid $C_6H_2.Cl_3.CH:CH.CO_2H$ [1:2:3:6]. [185°]. Formed by the action of acetic anhydride and sodium acetate on (β)-tri-chloro-benzoic aldehyde (Seelig, *A.* 237, 151).

CHLORO-CITRACONIC ACID $C_5H_5ClO_4$. The salts of this acid are formed from the anhydride. The free acid, liberated by the addition of H_2SO_4 to the barium salt, splits up at once into water and anhydride. Zn and HCl reduce it to pyrotartaric acid.

Salts.—CaA''.—$BaA''3\frac{1}{2}aq$.—$BaA''4aq$.—PbA''.—$AgHA''$.—Ag_2A''.

Anhydride $C_5H_3ClO_3$. [99°]. (212°). Formed by distilling citra-di-chloro-pyrotartaric or chloro-citramalic acid (Gottlieb, *J. pr.* [2] 8, 73; Swarts, *J.* 1873, 582). Laminæ; may be sublimed. Sl. sol. water, v. sol. alcohol and ether.

CHLORO-CITRIC ACID $C_6H_7ClO_7$. From aconitic acid and HOCl (Pawolleck, *A.* 178, 155). Unstable syrup. Boiling with water or baryta-water gives oxy-citric acid.

CHLORO-CODEINE *v.* Codeïne.

CHLORO- COMPOUNDS. *See also* Bromo-compounds. In organic compounds chlorine can displace hydrogen atom for atom, the resulting compound possessing as a rule considerable resemblance to the parent substance. This observation in the hands of Laurent and Dumas overthrew the electro-chemical theory of chemical affinity which had been established by Berzelius (*cf. K.* 1, 66). The hydrogen that is displaced by chlorine is usually that attached to carbon. Chlorination may be effected by a mixture of $KClO_3$ and HCl, by PCl_5, $SbCl_5$, or AcCl, but it is usually effected by the direct action of chlorine gas. The chlorination of aromatic hydrocarbons may be effected by heating the hydrocarbons with the theoretical amount of PCl_5 at 190°; in this case the PCl_5 splits up into PCl_3 and chlorine, the latter then attacking the side chains; the products are nearly pure (Colson a. Gautier, *Bl.* [2] 45, 6; *C. R.* 101, 1064). In the same way acetyl chloride heated for several weeks with PCl_5 in an open flask is converted into chlorinated acetyl chlorides (Michael, *Am.* 9, 215). Acetyl chloride itself may be used as a chlorinating agent; thus benzene-azo-benzene heated with AcCl at 170° for 4 hours is converted into *p*-chloro-benzene-azo-chloro-benzene and *p*-chloro-acetanilide (Becker, *B.* 20, 2006). When free chlorine is used the substitution is usually slow unless it is aided by daylight, by sunlight, by heat, or by carriers.

Sunlight enables chlorine to enter the side chains of aromatic hydrocarbons even at 0° (Schramm, *B.* 18, 1272), which it will otherwise only do at a high temperature; in the cold and in the dark it only enters the benzene nucleus. Chlorine enters the methyl group of acetophenone whether the action take place in daylight or in the dark; the chlorination is, however, much more rapid in daylight (Gautier, *C. R.* 104, 1714).

Carriers. Iodine greatly assists chlorination, probably forming ICl_3, which reacts more vigorously than chlorine alone (Hugo Müller, *C. J.* 15, 41). The chlorides of metals which form two chlorides also act as carriers; *e.g.* $SbCl_5$ (Hugo Muller; Beilstein a. Geitner, *A.* 139, 334; Ruoff, *B.* 9, 1486), $MoCl_5$ (Aronheim, *B.* 8, 1400; 9, 1788; Page, *A.* 225, 199), Fe_2Cl_6, Al_2Cl_6, TlCl, and the chlorides of Au, Sn, Bi, S, Te, Ga, Zr, Nb, In, Ta, and Ur. On the other hand the chlorides of Na, K, Li, Ag, Cu, Ca, Ba, Sr, Mg, Zn, Hg, B, P, As, Se, Y, Ce, and Di, are not carriers (Willgerodt, *J. pr.* [2] 34, 264; 35, 398) According to Page, however, the chlorides of Sn, S, and Bi are not carriers, as is also the case with the chlorides of Ti, Cr, W, Mn, Co, and Ni. It is, however, not possible to draw an absolute line of demarcation between carriers and non-carriers; the weaker carriers can only attack substances prone to chlorination. The effect of various chlorides is modified by circumstances, such as their solubility in the substance to be chlorinated, their stability in presence of water, and the temperature of the reaction. $MoCl_5$ acts as a carrier of chlorine to aromatic bodies only and not to fatty compounds. It may be supposed that these various carriers act by alternately giving up chlorine to the compound and taking it up again:

$$C_6H_6 + MoCl_5 = C_6H_5Cl + MoCl_3 + ClH$$
$$MoCl_3 + Cl_2 = MoCl_5.$$

This does not account for the fact that carriers promote entrance into the benzene nucleus, nor for the observation that no ferrous chloride is formed when benzene is heated with Fe_2Cl_6. An alternative supposition is that in the case of aromatic bodies a molecular compound is first formed, possibly aided by the somewhat unsaturated condition of the benzene ring, and that this molecular compound is subsequently decomposed by chlorine.

Displacement of one halogen by another. Iodo- compounds may be converted into chloro- compounds by digestion with $HgCl_2$; on the other hand, chloro- compounds may be changed to iodo- compounds by treatment with KI or, better, $CaI_2 3\frac{1}{2}H_2O$. Even acetyl chloride may be converted into acetyl iodide by heating with crystallised calcium iodide, without being affected by the water of crystallisation. In general, metals with low atomic weights prefer the lighter halogens. The following elements prefer chlorine to bromine or iodine, and bromine to iodine; viz., K, Mg, Ca, Sr, Ba, Al, Mn, Co.

On the other hand, Cu, Ag, Hg, Sn, Pb, As, and Sb prefer iodine to bromine or chlorine, and bromine to chlorine. P and Ti are indifferent. The metals Zn, Cd, Tl, Bi, Fe, and Ni are variable in their behaviour (Kohnlein, *A.* 225, 194).

Thus *n*-propyl iodide is not acted on by $MgCl_2$, $SrCl_2$, or $BaCl_2$; it is split up into gas and HI by $MnCl_2$ and $TiCl_4$; it is but slightly affected by $FeCl_2$, $CoCl_2$, and $NiCl_2$; but it is converted into propyl chloride by $ZnCl_2$, $CdCl_2$, $SnCl_4$, $SnCl_2$, $SbCl_3$, and TlCl.

n-Propyl chloride is converted into propyl iodide by CaI_2, SrI_2, MnI_2, and CoI_2; is but slightly affected by FeI_2 and NiI_2; and is not affected by SnI_2.

The substitution of chlorine by iodine may be effected by the use of KI in the case of chloro-lactic acid, chloro-acetone, di-chloro-acetone, epichlorhydrin, and dichlorhydrin; on the other hand, KI does not act on dichlorinated ethyl oxide, and decomposes chloral into chloroform and CO.

The substitution of Cl by I may be effected by Al_2I_6 in the case of CCl_4 and $CH_3.CHCl_2$; but Al_2I_6 does not act on C_6Cl_6 or on C_2Cl_4, while it splits up C_2Cl_6 into C_2Cl_4 and Cl_2.

KBr converts di-chloro-acetone into di-bromo-acetone. Al_2Br_6 converts CCl_4, C_2Cl_4, and C_2Cl_6 into CBr_4, C_2Br_4, and C_2Br_6 respectively.

The conversion of EtI into EtCl is not effected by $BaCl_2$, $CuCl_2$, or $PbCl_2$ at 72°, but is partially brought about by $BaCl_2$ at 140°, and is completely effected by $CuCl_2$ and $PbCl_2$ at 160°. The observation of Henry (*C. R.* 96, 1062) that silver nitrate converts ethylene chlorobromide $CH_2Cl.CH_2Br$ into chloro-ethyl nitrate $CH_2Cl.CH_2O.NO_2$ is in accordance with the statement made above, that silver prefers bromine to chlorine. Chlorine may be displaced by iodine by heating with conc. HIAq in sealed tubes, but the resulting iodo- compound is, especially in the case of aromatic compounds, liable to loss of iodine in exchange for hydrogen; thus chloro-benzenes are reduced to benzene by HI at 250° without any iodo-benzenes being formed (Berthelot, *Bl.* [2] 9, 30).

Chlorinated hydrocarbons.

Formation.—1. By chlorination of hydrocarbons. Chlorine enters the ω and α positions in fatty hydrocarbons; thus *n*-pentane gives

$$CH_3.CH_2.CH_2.CH_2.CH_2Cl$$

and $CH_3.CH_2.CH_2.CHCl.CH_3$. On further chlorination, the chlorine turns out hydrogen that is attached to the same atom of carbon as the chlorine atom already present. In the case of aromatic hydrocarbons chlorine enters the side chain only at a high temperature or in sunlight. In presence of iodine or $SbCl_5$ it enters the benzene nucleus even at boiling temperature (*v. supra*). The rules relating to substitution in the benzene nucleus are given in the article BENZENE. The displacing action of chlorine is not confined to hydrogen; thus it can convert nitro-benzene into C_6Cl_6 (Page, *A.* 225, 208).—2. Mono-chlorinated hydrocarbons or alkyl chlorides are formed by treating alcohols with HCl, PCl_5, PCl_3, or $POCl_3$. The action of HCl on alcohols is promoted by $ZnCl_2$ (Groves, *C. J.* 27, 636; *A.* 174, 372; Krüger, *J. pr.* [2] 14, 195), but in the case of the higher fatty alcohols the resulting chloride is sometimes mixed with an isomeride derived from the olefine formed by dehydration of the alcohol (Schorlemmer, *C.J.* 28, 308; *B.* 7, 1792). The polyhydric alcohols will not exchange all their hydroxyls for Cl by treatment with HCl but require the use of PCl_5.—3. From olefines and HCl; the chlorine attaching itself to the atom of carbon that is combined with the fewer hydrogen atoms. Di-chlorinated hydrocarbons are formed by the union of Cl with olefines, or of HCl with the hydrocarbons C_nH_{2n-2}. Although chlorine combines with olefines in the dark, its combination with benzene and acetylene requires light (Romer, *A.* 233, 172).—4. From aldehydes or ketones and PCl_5. 5. From aromatic amines by the diazo- reaction (*v.* DI-AZO-COMPOUNDS and AMINES). The conversion may also be effected by gradually adding HNO_2 to a hot solution of the amine in HCl (Losanitsch, *B.* 18, 39).

Reactions.—1. Boiling *water* very slowly decomposes chlorinated hydrocarbons; the chlorides of tertiary alkyls are the most readily affected (Niederist, *A.* 186, 388). Presence of $Pb(OH)_2$ or K_2CO_3 in the water promotes the conversion of chlorinated hydrocarbons into alcohols. If two chlorine atoms are attached to the same carbon atom, the product is an aldehyde or ketone; if three are attached to the same carbon atom, the product is an acid.—2. *Ammonia* converts the alkyl chlorides into amines. 3. *Alcoholic potash* removes HCl in two stages from di-chlorinated hydrocarbons, the Cl and H being detached from neighbouring carbon atoms, the hydrogen coming from the carbon atom to which the less hydrogen is attached.—4. Chlorine may be displaced by hydrogen by treatment with sodium-amalgam in presence of dilute alcohol; with zinc-dust and HOAc; or with conc. HIAq. 5. Dry *oxalic acid* displaces chlorine by oxygen in the compounds $RCHCl_2$ and $RCCl_3$ (Anschutz, *A.* 226, 13).

Chlorinated acids.

Formation.—1. By direct chlorination; chlorine taking the α position if possible, especially if the temperature be not above 100° (Erlenmeyer, *B.* 14, 1318).—2. From salts of oxy-acids and PCl_5, the resulting chlorinated alkoyl chloride being decomposed by water.—3. By addition of chlorine or of HCl to unsaturated acids; HCl uniting with acids of the form $RCH:CH.CO_2H$ gives rise chiefly to β-chloro-acids $RCHCl.CH_2.CO_2H$.

Reactions.—1. Boiling with *water* or alkalis usually converts α-chloro-acids into oxy-acids, β-chloro-acids into unsaturated acids, and γ-chloro-acids into lactones. The β-chloro-acids also split up into HCl, CO_2, and an olefine (Fittig, *A.* 195, 169; *cf.* Erlenmeyer, *B.* 14, 1318; 15, 49). KOEt converts α-chloro-acids into ethoxy-acids. αα-di-chloro-acids are but slightly affected by boiling water; αβ-di-chloro-acids give the chloro-oxy-acid, and also split off CO_2. Alcoholic KOH converts acids of the form $RCHCl.CHCl.CO_2H$ chiefly into $RCH:CCl.CO_2H$.

Acid chlorides.

Formation.—1. By the action of PCl_5, PCl_3, or $POCl_3$ on the acid or on a dry salt of the acid (Gerhardt, *A.* 87, 63; Béchamp, *C. R.* 40, 944; Kanonnikoff, *A.* 175, 378). Although PCl_5 does not convert tri-chloro-methane-sulphonic acid into its acid chloride, it acts upon methane sulphonic acid and chloro-methane sulphonic acid in the usual way.—2. By the action of HCl on a mixture of the acid and P_2O_5 (Friedel, *Z.* 1869, 489).

Reactions.—1. Quickly decomposed by *water* into HCl and the corresponding acid, and even more readily decomposed by *alcohols* with formation of ethers.—2. *Ammonia* forms amides; primary *amines* act similarly.—3. *Salts of organic acids* form anhydrides. Dry *oxalic acid* also converts them into anhydrides (Anschütz, *A.* 226, 13; *v.* Anhydrides, Organic).—4. *Zinc ethyl* unites with them forming compounds such as $R.C(OZnEt)EtCl$ which are converted by water into ketones $R.CO.Et$; further action of zinc ethyl forms $R.C(OZnEt)Et_2$ whence water forms tertiary alcohols $R.C(OH)Et_2$. Thus $CO_2Et.COCl$ becomes $CO_2Et.C(OH)Et_2$ (Henry, *B.* 5, 949).—5. *Aluminium chloride* forms with acetyl chloride diluted with CS_2 a white solid $C_{12}H_{14}O_6Al_2Cl_8$ decomposed by water into $CH_3.CO.CH_2.CO.CH_3$ with evolution of CO_2, and by alcohol into acetyl-aceto-acetic ether. Al_2Cl_6 acts similarly on chlorides of other normal fatty acids (Combes, *A. Ch.* [6] 12, 199).—6. *Chlorine* acts by substitution more vigorously upon acid chlorides than upon the acids themselves (Jazukowitzsch, *Z.* 1868, 234).—7. *Sodium amalgam* added to a mixture of an acid with its chloride reduces the latter to the corresponding alcohol (Linnemann, *A.* 161, 184; Baeyer, *B.* 2, 98).

Chloroamides and chloroimides $R'.NHCl$, $R'_1R'_2NCl$, $R''NCl$ where R′, R'_1, and R″ are acid radicles, and R'_2 acid or alcoholic.

These bodies are formed by adding a conc. solution of chloride of lime to the solution of the amide or imide acidified with AcOH.

By treatment with alkalis, HCl, &c., their Cl atom is readily replaced by H (Bender, *B.* 19, 2272).

CHLORO-CONIINE *v.* Coniine.

(α)-CHLORO-COUMARIN $C_9H_5ClO_2$. [123°]. From coumarin and PCl_5 at 200°. Also from coumarin dichloride and alcoholic KOH (Perkin, *C. J.* 24, 43). Flat needles, m. sol. alcohol, sl. sol. hot water. Converted by alcoholic KOH into coumarilic acid.

(β)-Chloro-coumarin $C_9H_5ClO_2$. [162°]. From Ac_2O and sodium chloro-*o*-oxy-benzoic aldehyde $C_6H_3Cl(ONa)CHO$ (Bäsecke, *A.* 154, 85). Crystals, sl. sol. cold alcohol, v. e. sol. benzene. Boiling KOHAq converts it into chloro-coumaric acid.

Tetra-chloro-coumarin $C_9H_2Cl_4O_2$. [145°]. Formed by passing chlorine into coumarin dissolved in CCl_4 containing iodine (P.). Small needles (from alcohol).

CHLORO-*p*-CRESOL $C_6H_3(CH_3)Cl(OH)$ [1:3:4] (196°). S.G. $\frac{25}{25}$ 1·2106. Formed by the action of dry chlorine on sodium-*p*-cresol (Schall a. Dralle, *B.* 17, 2528). Liquid.

Methyl ether $C_6H_3MeCl(OMe)$. (214°). S.G. $\frac{25}{25}$ 1·1493. Liquid.

Chloro-cresol $C_6H_3(CH_3)Cl(OH)$ or $C_6H_4(CH_2Cl)(OH)$. [56°]. (c. 240°). Formed by chlorination of boiling crude cresol (Biedermann, *B.* 6, 325). Needles; v. sol. alcohol, ether, and benzene.

Chloro-cresol. *Ethyl ether* $C_6H_3MeCl(OEt)$. (c. 215°). S.G. $^{19.5}$ 1·127. From (α)-chloro-nitro-toluene by reduction, diazotisation, and treatment of the diazo-sulphate with boiling alcohol (Wroblewsky, *A.* 168, 209).

Chloro-cresol. *Ethyl ether* $C_6H_3MeCl(OEt)$. (c. 215°). S.G. ^{18} 1·131. From (β)-chloro-nitro-toluene in the same way as the preceding (W.).

Di-chloro-*p*-cresol $C_6H_2(CH_3)Cl_2(OH)$ [39° uncor.]. Formed by passing chlorine into boiling *p*-cresol (Claus a. Riemann, *B.* 16, 1598). Long prismatic needles. Sol. alcohol and ether, sl. sol. hot water. By CrO_3 in acetic acid it is oxidised to di-chloro-*p*-oxy-benzoic acid [156° uncor.]. $-A'NH_4$: long colourless needles [125°], sublimable.

Di-chloro-*m*-cresol $C_6H_2(CH_3)Cl_2(OH)$; probably [1:4:6:3]. [46° uncor.]. Formed by chlorinating *m*-cresol (Claus a. Schweitzer, *B.* 19, 930). Colourless needles. Volatile with steam. V. e. sol. alcohol, ether, &c., sol. hot water, nearly insol. cold. It is oxidised by $K_2Cr_2O_7$ and dilute H_2SO_4 to di-chloro-toluquinone [103°].

Di-chloro-*o*-cresol $C_6H_2(CH_3)Cl_2(OH)$ [1:5:3 or 4:2] [54° uncor.]. Formed by chlorination of *o*-cresol (C. a. R., *B.* 16, 1600). Large colourless needles. V. sol. alcohol, ether, benzene, chloroform and CS_2, sol. hot water, sl. sol. cold water. By CrO_3 and glacial acetic acid it is oxidised to a mixture of di- and tri-chloro-toluquinone. By $K_2Cr_2O_7$ and dilute H_2SO_4 it is oxidised to mono-chloro-toluquinone [90°] (Claus a. Schweitzer, *B.* 19, 927).

***Exo*-Di-chloro-*o*-cresol** $C_6H_4(CHCl_2)(OH)$ [1:2]. [82°]. From salicylic aldehyde (1 mol.) and PCl_5 (1 mol.) (Henry, *B.* 2, 135). Prisms (from ether); v. sl. sol. cold alcohol.

Phosphoryl derivative $PO(O.C_6H_4.CHCl_2)_3$. [78°]. From salicylic aldehyde and PCl_5 (Stuart, *C. J.* 53, 402). Needles (from alcohol). Not affected by boiling dilute NaOH Aq.

Methyl ether $C_6H_4(CHCl_2)(OMe)$. (231°). From $C_6H_4(OMe)CHO$ [1:2] and PCl_5 (Stuart, *C. J.* 53, 401). Oil. Decomposed in moist air.

Tri-chloro-cresol $C_6H(CH_3)Cl_3(OH)$. [96°]. (270°). One of the products of distillation of crude penta-chloro-thymol (Lallemand, *J.* 1856, 620). Crystals; insol. water, sol. alcohol and alkalis.

Tetra-chloro-cresol $C_6(CH_3)Cl_4(OH)$. [150°]. Obtained by distilling pure penta-chloro-thymol (L.). Needles.

α-CHLORO-CROTONIC ACID
$CH_3.CH:CCl.CO_2H$. [97·5°]. (206°) (Kahlbaum, *B.* 12, 2335); (212°) (Sarnow). S. 1·97 at 12° (K.); 2·12 at 19° (Michael a. Brown, *Am.* 9, 283).

Formation.—1. From tri-chloro-butyric aldehyde by oxidation and treatment of the resulting tri-chloro-butyric acid with zinc and HCl (Krämer a. Pinner, *A.* 158, 37) or with zinc-dust and water (Sarnow, *A.* 164, 93; *B.* 4, 731; 5, 467). 2. By boiling tri-chloro-butyric aldehyde (29 g.) with K_4FeCy_6 (42 g.) and water (500 g.) (Wallach, *B.* 10, 1530).—3. From solid crotonic acid by addition of chlorine followed by heating the product $CH_3.CHCl.CHCl.CO_2H$ (Friedrich, *A.* 219, 373). 4 From chloro-butenyl alcohol (*q. v.*) by oxidation. -5. By the action of cold aqueous NaOH upon the liquid *allo*-αβ-di-chloro-butyric acid (the addition product of isocrotonic acid and Cl) (Wislicenus, *B.* 20, 1009).

Properties.—Small flat needles; may be sublimed. Volatile with steam. Not attacked by alkalis below 220°, at which temperature acetic and oxalic acids are formed, together with CO_2 and a syrupy acid (F.). Reduced by sodium-amalgam to crotonic acid.

Salts. -A'K: pearly plates or tables (from 80 p.c. alcohol); nearly insol absolute alcohol. - NH_4A'; laminæ. - CaA'_2. - BaA'_2: laminæ. — PbA'_2 aq. - CuA'_2: needles. CuA'(OH): amorphous.— AgA': needles.

Methyl ether MeA'. (161°). S.G. $^{\underline{4}}$ 1·0933 μ_D 1·4589 (Kahlbaum, *B.* 12, 344).

Ethyl ether EtA'. (177° uncor.). S.G. $^{\underline{15}}$ 1·129. From tri-chloro-butyric aldehyde and alcoholic KCN (Wallach a. Böhringer, *A.* 173, 301, *cf.* Claus, *A.* 191, 63). Turns brown in light.

Reactions. -1. Treated with KCN (2 mol.) and boiling alcohol it forms a product whence boiling KOH produces tri-carballylic acid (Claus, *A.* 191, 64) and crotaconic acid, $C_4H_4(CO_2H)_2$, isomeric with itaconic acid. The tricarballylic acid is formed through addition of HCN to the crotaconic acid.—2. With KCN (2 mol.) and dilute alcohol in the cold it forms potassic cyano-crotonate (*q. v.*) only.

Chloride.—$CH_3.CH:CCl.COCl$. (142°). (S.).

Amide $CH_3.CH:CCl.CO.NH_2$ [112°] (P. a. K.); [107°] (S.). (c. 235°) (S.). From the cyanhydrin of tri-chloro-butyric aldehyde and alcoholic NH_3 or dry ammonium carbonate (Pinner a. Klein, *B.* 11, 1488). Also from the chloride and NH_3 (S.). Laminæ; may be sublimed.

Nitrile $CH_3.CH:CCl.CN$. (136°). From the amide and P_2O_5 (S.).

***Allo*-α-chloro-crotonic acid** $CH_3.CH:CCl.CO_2H$. [67°]. S. 6·53 at 19°. Formed by the action of an excess of aqueous NaOH upon αβ di-chloro-butyric acid [63°] at the ordinary temperature (Wislicenus, *B.* 20, 1009; Michael a. Brown, *Am.* 9, 283). Slender needles (from water). More soluble in water than any of the other chloro-crotonic acids; sl. sol. cold ligroïn.—A'K: concentric needles, v. sol. absolute alcohol (difference from the α-acid, whose K salt is nearly insoluble).—BaA'_2 3½ aq: crystals, sl. sol. alcohol. - PbA'_2 aq: prisms, sl. sol. water. - AgA': amorphous.

β-Chloro-crotonic acid $CH_3.CCl:CH.CO_2H$. [94·5°]. (c. 209°) S. 1·9 at 19° (Michael a. Brown, *Am.* 9, 283); 2·25 at 12° (K.); 2·8 at 19° (G.).

Formation.—1. The chloride of this acid is formed together with that of *allo*-β-chloro-crotonic acid by the action of excess of PCl_5 on aceto-acetic ether. The mixed chlorides are saponified by water and the product distilled, whereupon β-chloro crotonic acid passes over first (Geuther, *Z.* 1871, 237).—2. From tetrolic acid and fuming HCl (Friedrich, *A.* 219, 370).

Properties.—Slender monoclinic needles; $a:b:c = 1·2859:1:·6105$; $\beta = 73° 9'$; volatile with steam; may be sublimed at 100°. At 160° it slowly changes into *allo*-β-chloro-crotonic acid.

Reactions.—1. *Sodium amalgam* gives crotonic acid. -2. Boiling *aqueous potash* (7 p.c.) gives tetrolic acid (K.). Stronger potash (18 p.c.) gives chiefly acetone.—3. *Sodium ethylate* gives the same ethoxy-crotonic acid as is got from *allo*-β-chloro-crotonic acid.

Salts.—NaA' ½aq: thin laminæ, v. e. sol. water.—BaA'_2: trimetric octahedra. S. 45 at 18°. —CuA'_2 aq.

Ethyl ether EtA'. (184° cor.). S. G. $^{\underline{16\cdot5}}$ 1·111 (G.).

***Allo*-β-chloro-crotonic acid**
$CH_3.CCl:CH.CO_2H$. [59·5°]. (195° cor.). S. 1·12 at 7°. Formed from aceto-acetic ether as above described (Geuther a. Fröhlich, *Z.* 1869, 270). Formed also by heating the preceding acid for 20 hours at 160° (Friedrich, *A.* 219, 363).

Properties. Slender needles or prisms; volatile with steam; sublimes even at 20°. Not affected by boiling aqueous KOH.

Reactions.—1. Alcoholic KOH converts it into the ethyl derivative of *allo*-β-oxy-crotonic acid.—2. Conc. KOHAq forms acetone and CO_2, a small quantity of tetrolic acid $C_4H_4O_2$ [75°–77°] being also formed (Friedrich, *A.* 219, 341). Dilute KOH behaves similarly, but the tetrolic acid is the chief product.

Salts. -NaA' ½aq: satiny crystals, v. sol. water. — KA'aq. — TlA' ½aq. $NH_4HA'_2$ aq. — CaA'_2 3aq. BaA'_2 2aq: four-sided prisms. - $MgA'_2$5aq. —$ZnA'_2$2½aq. $PbA'_2$4aq. —$MnA'_2$2aq. —$CoA'_2$6aq. -NiA'_2 6aq. -CuA'_2 1½aq. AgA'.

Methyl ether MeA'. (142° cor.). S.G. $^{\underline{15}}$ 1·113.

Ethyl ether EtA'. (161° cor.). S.G. $^{\underline{15}}$ 1·113. Boiling alcoholic KCN followed by KOH converts it into tri-carballylic acid (Claus a. Lischke, *B.* 14, 1089).

Isomeride of chloro-crotonic acid *v.* CHLORO-METHACRYLIC ACID.

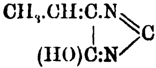
αβ-Di-chloro-crotonic acid
$CH_3.CCl.CCl.CO_2H$. From ααβ-tri-chloro-butyric acid (1 mol.) and KOH (2 mols.) (Garzarolli, *B.* 9, 1209).

α-CHLORO-CROTONIC ALDEHYDE
$CH_3.CH:CCl.CHO$. (140°). Formed, together with tri-chloro-butyric aldehyde, by chlorinating aldehyde containing alcohol (Pinner, *A.* 179, 31). Formed also by heating the hydrate of chloro-

acetic aldehyde with aldehyde and a drop of fuming HCl at 100° (Lieben a. Zeisel, *M.* 4, 531). Liquid. Combines with chlorine forming tri-chloro-butyric aldehyde. Br gives chloro-di-bromo- and chloro-tri-bromo- butyric aldehydes (Pinner, *B.* 8, 1323).

$\alpha\gamma$-**Di-chloro-butyric aldehyde** $CH_2Cl.CH:CCl.CHO$. (86°) at 18 mm. Gradually separates as an oil when the hydrate of chloro-acetic aldehyde is heated with a drop of H_2SO_4 at 100° (Natterer, *M.* 4, 539; 5, 567). Oil; solidifies when cooled with solid CO_2. Forms a crystalline compound with $NaHSO_3$. Reduces warm ammoniacal $AgNO_3$. Reduced by iron filings and acetic acid to *n*-butyl and butenyl alcohols. Oxidised by HNO_3 to oxalic and chloro-acetic acids. Br forms $\alpha\gamma$-di-chloro-$\alpha\beta$-di-bromo-butyric aldehyde. HCl gives tri-chloro-butyric aldehyde. $ZnEt_2$ followed by dilute H_2SO_4 gives a di-chloro-hexenyl alcohol $C_6H_{10}Cl_2O$ (c. 117°) at 20 mm.

CHLORO-CROTONYL-UREA $CH_3.CH:CCl.CO.NH.CO.NH_2$. [224°]. The chief product of the reaction of the cyanhydrin of tri-chloro-butyric aldehyde with urea; the yield is about 60 p.c. Rhombic tables. Sol. alcohol. sl. sol. water. On heating it evolves HCl and is converted into di-oxy-ethylidene-metapyrazole



$$\begin{array}{l}CH_3.CH:C.N\\ \quad\;\;|\qquad\quad\;\;\rangle C(OH)\\ \;(HO)C:N\end{array}$$

(Pinner a. Lifschütz, *B.* 20, 2347).

CHLORO-CROTYL *v.* CHLORO-BUTENYL.

CHLORO-ψ-CUMENE $C_6H_2(CH_3)_3Cl$ [1:3:4:6]. [71°]. White plates. Formed by the action of cuprous chloride upon diazo-pseudo-cumene (Haller, *B.* 18, 93) or by warming the piperidide of diazo-pseudo-cumene with conc. HClAq (Wallach a. Heusler, *A.* 243, 232).

ω-**Chloro** *n*-**cumene** $C_9H_{11}Cl$ *i.e.* $C_6H_5.CH_2.CH_2.CH_2Cl$. *Chloro-propyl-benzene.* (219°). From $C_6H_5.CH_2.CH_2.CH_2OH$ and HCl (Errera, *G.* 16, 310). Oil. Not affected by fused $ZnCl_2$ nor by AgOAc. Alcoholic KOH gives $C_6H_5.C_3H_6.OEt$ (220°).

α-**Chloro-*n*-cumene** $C_6H_5.CH_2.CHCl.CH_3$. (c. 206°). From $C_6H_5.CH_2.CH(OH).CH_3$ and HCl (E.). Formed also by chlorination of *n*-propyl-benzene (Errera, *G.* 14, 506). Partially decomposed by distillation into HCl and allyl-benzene. Alcoholic KOH also forms allyl-benzene, as does $ZnCl_2$ likewise.

β-**Chloro-*n*-cumene** $C_6H_5.CHCl.CH_2.CH_3$. (c. 203°). From the corresponding phenyl-propyl alcohol and HCl (E.). Partially resolved by distillation, even *in vacuo,* into HCl and allyl-benzene. AgOAc forms $C_6H_5.CH(OAc).CH_2.CH_3$ (227°).

CHLORO-CUMINIC ACID $C_{10}H_{11}ClO_2$ *i.e.* $C_3H_7.C_6H_3Cl.CO_2H$ [4:3:1]. [123°]. Formed by oxidation by HNO_3 of the chloro-cymene from thymol and PCl_5 (Gerichten, *B.* 11, 365; Fileti a. Crosa, *G.* 16, 288). Long needles (from dilute alcohol). Reduced to cuminic acid by sodium-amalgam. – BaA'_2 3aq: pearly plates.

CHLORO-CUMOQUINOLINE *v.* CHLORO-ISO-PROPYL-QUINOLINE.

CHLORO-CYANAMIDE *v.* AMMELINE.

CHLORO-CYANO-BENZENE *v. Nitrile of* CHLORO-BENZOIC ACID.

CHLORO-DI-CYANO-NITRO-METHANE $CClCy_2(NO_2)$. Formed by warming chloropicrin with alcoholic KCy (Basset, *C. J.* 19, 352). Silver nitrate solution gives an orange pp. of $(AgNO_3)_4 3CClCy_2(NO_2)$.

CHLORO-CYMENE $C_{10}H_{13}Cl$ *i.e.* $C_6H_3MePrCl$ [1:4:2]. (210°). S.G. ^{14} 1·014. From carvacrol and PCl_5 (Kekulé a. Fleischer, *B.* 6, 1090). Formed also by chlorination of cymene (from camphor) in presence of iodine (v. Gerichten, *B.* 10, 1249). Oxidised by dilute HNO_3 to chloro-toluic acid [196°].

Chloro-cymene $C_6H_3MePrCl$ [1:4:3]. (213°). From thymol (4 mols.) and PCl_5 (1 mol.); the yield being 85 p.c. (Carstanjen, *J. pr.* [2] 3, 64; v. Gerichten, *B.* 10, 1250; 11, 365; Fileti a. Crosa, *G.* 16, 287). Not affected by sodium amalgam (F. a. C.). Oxidation gives chloro-cuminic [117°], chloro-toluic [149°], and chloro-terephthalic, acids.

ω-**Chloro-cymene** $C_6H_4Pr(CH_2Cl)$ [1:4]. *Cumyl chloride.* (c. 227°). Formed by passing chlorine into boiling cymene (Errera, *G.* 14, 277). Decomposed by long boiling with formation of $C_{20}H_{24}$. Alcoholic KOH gives $C_{10}H_{13}OEt$. Sodium amalgam reduces it to cymene. Boiling aqueous $Pb(NO_3)_2$ gives cuminic aldehyde.

Exo-**chloro-cymene** $C_6H_4(C_3H_6Cl)Me$ [1:4]. Two compounds of this nature are formed, together with the preceding body, on passing chlorine into boiling cymene (derived from camphor). One of them is not attacked by alcoholic KOH, while the other is converted into allyl-toluene $C_6H_4(C_3H_5)Me$ (Errera, *G.* 14, 283).

ω-**Chloro-*p*-isocymene** $C_6H_4Pr(CH_2Cl)$ [1:4]. *Cumyl chloride.* (c. 230°). Formed, together with cumyl carbamate, by passing cyanogen chloride into cuminyl alcohol $C_6H_4Pr.CH_2OH$ (Spica, *G.* 5, 394). Formed also by the action of HCl on cuminyl alcohol (Paterno a. Spica, *G.* 9, 397; *B.* 12, 2366).

$\omega\omega$-**Di-chloro-cymene** $C_6H_4(C_3H_7).(CHCl_2)$. *Cumylidene chloride.* (c. 258°). From cuminic aldehyde and PCl_5 (Cahours, *A.* 70, 44; *Suppl.* 2, 311; Sieveking, *A.* 106, 258). Reconverted by alcoholic KOH or by heating with water at 150° into cuminic aldehyde.

Tetra-chloro-*m*-isocymene C_6Cl_4PrMe [1:3]. [159°]. Formed by passing chlorine into a cold saturated solution of tri-chloro-isocymene sulphonic acid at 40° (Kelbe, *B.* 16, 617). Needles (from alcohol); may be sublimed. Not oxidised by HNO_3 or chromic mixture.

TRI-CHLORO-*m*-ISOCYMENE SULPHONIC ACID $C_6Cl_3PrMe(SO_3H)$. From *m*-isocymene sulphonic acid by passing Cl into its aqueous solution at 40° (Kelbe, *B.* 16, 618).—NaA': laminæ.

CHLORO-DECANE *v.* DECYL CHLORIDE.

CHLORO-DECYLENE $C_{10}H_{19}Cl$. (206° cor.). From Cl and boiling decanaphthene (Markownikoff a. Ogloblin, *J. R.* 15, 333). Alcoholic KOH gives a mixture of decinenes (155°–165°).

TETRA-CHLORO-DURENE $C_6H_2(CH_2Cl)_4$ [1:2:4:5]. [144°]. S.G. 1·479. Formed by heating durene with excess of PCl_5 at 190° for 5 hours (Colson a. Gautier, *C. R.* 102, 1075; *Bl.* [2] 46, 198).

DI-CHLORO-EOSIN *v.* DI-CHLORO-TETRA-BROMO-FLUORESCEIN.

CHLORO-ETHANE *v.* ETHYL CHLORIDE.

Di-chloro-ethane *v.* ETHYLENE CHLORIDE and ETHYLIDENE CHLORIDE.

Tri-chloro-ethane $CH_2Cl.CHCl_2$. *Chloro-ethylene chloride.* (114°) (Schiff, *A.* 220, 97); (115°) (Perkin, *C. J.* 45, 531). V.D. 4·66 (for 4·60). S.G. $\frac{94}{4}$ 1·4577; $\frac{15}{15}$ 1·4553; $\frac{25}{25}$ 1·4430. M.M. 6·796 at 16·7°. C.E. (from 9° to 113°) ·00121. H.F.p. 33980 (*Th.*). H.F.v. 32820. S.V. 102·77.

Formation.—1. From chloro-ethylene (vinyl chloride) and $SbCl_5$ (Regnault, *A. Ch.* [2] 69, 151; 71, 355).—2. From ethyl chloride and Cl (Krämer, *B.* 3, 261).—3. By chlorinating ethylidene chloride in presence of Al_2Cl_6 (Tavildaroff, *B.* 13, 2403).—4. From $CHCl_2.CH_2OH$ and PCl_5 (de Lacre, *C. R.* 104, 1186).

Reactions.—1. Aqueous or alcoholic *ammonia* gives a theoretical yield of $C_2H_2Cl_2$ (37°) (Engel, *C. R.* 104, 1621); alcoholic KOH forms the same body.—2. *Sodium* forms C_2H_4, $C_2H_2Cl_2$, C_2H_2, and hydrogen (Brünner a. Brandenburg, *B.* 10, 1496; 11, 61).

Tri-chloro-ethane $CH_3.CCl_3$. (76°) (Perkin); (74·5°) (Geuther). V.D. 4·53. S.G. $\frac{15}{15}$ 1·3247; $\frac{25}{25}$ 1·3114. M.M. 6·740 at 17·6° (Perkin); ^{0} 1·347 (Pierre, *A.* 80, 127). Formed by chlorinating ethyl chloride (Regnault, *A.* 33, 317; Geuther, *J.* 1870, 435). Converted by NaOEt at 100° into CH_2:CCl(OEt), acetic acid, and ortho-acetic ether $CH_3.C(OEt)_3$. Differs from its isomeride in forming, when cooled, with aqueous H_2S, a crystalline compound $C_2H_3Cl_32H_2S$ 23aq (Forcrand, *A. Ch.* [5] 28, 25).

***u*-Tetra-chloro-ethane** $CH_2Cl.CCl_3$. (135°) (Regnault); 139° (Pierre, *A.* 80, 130); (130·5° i. V.) (Staedel, *B.* 15, 2563). S.G. ^{0} 1·6116 (P.); ^{12} 1·576. Formed by chlorinating ethylene chloride (Laurent, *A.* 22, 292) or $CHCl.CHCl_2$ (R.). With NaOEt it gives CHCl:CCl(OEt) and $CH_2(OEt).CO_2Na$. H_2S gives $C_2H_2Cl_42H_2S$ 23aq.

***s*-Tetra-chloro-ethane** $CHCl_2.CHCl_2$. *Acetylene tetrachloride.* (147° cor.). S.G. ^{0} 1·614 (P. a. P.); $\frac{0}{0}$ 1·5897 (Kanonnikoff).

Formation.—1. By passing acetylene into $SbCl_5$, which slowly absorbs it and deposits $C_2H_2SbCl_5$, the mixture of this body with $SbCl_5$ is then distilled (Berthelot a. Jungfleisch, *C. R.* 79, 542).—2. By passing acetylene into PCl_5; explosion often occurring (Sabanejeff, *A.* 216, 262).—3. By heating ethylene chloride with the calculated quantity of PCl_5 for ten hours at 190° (Colson a. Gautier, *C. R.* 102, 1075).—4. From di-chloro-acetic aldehyde and PCl_5 (Paternò a. Pisati, *G.* 1, 461; *J.* 1871, 508).

Properties.—Not affected by boiling water. Slowly decomposed at 360° giving HCl and hexa-chloro-benzene.

Penta-chloro-ethane $CHCl_2.CCl_3$. (158·9°) (Thorpe). S.G. $\frac{0}{4}$ 1·70893. C.E. (0°–10°) ·000949; (0°–100°) ·0009944. S.V. 138·2.

Formation.—1. From chlorine and EtCl (Regnault, *A.* 33, 321).—2. By chlorinating ethylene chloride (Pierre, *A.* 80, 130).

Preparation.—PCl_5 (190 g.) is gradually added to chloral (113 g.), boiled with inverted condenser and distilled. The portion distilling below 170° is washed with water, dried with $CaCl_2$ and rectified. The yield is small (Paternò *C. R.* 68, 450; Thorpe, *C. J.* 37, 192).

Properties.—Liquid, solidifies below −18°. Converted by alcoholic KOH into KCl and C_2Cl_4. PCl_5 at 250° gives C_2Cl_6.

Hexa-chloro-ethane $CCl_3.CCl_3$. [179°] (Geuther a. Brockhoff, *J. pr.* [2] 7, 108); [185° cor.] (Hahn, *B.* 11, 1735). (185° cor.) (H.). S.G. 2·0 (Schröder, *B.* 13, 1070). V.D. 8·16 (calc. 8·21).

Formation.—1. From C_2Cl_4 and Cl in daylight or by heating (Faraday, *Tr.* 1826, 47; Liebig, *A.* 1, 219).—2. The ultimate product of the chlorination of ethyl chloride (Laurent, *A. Ch.* [2] 84, 328) or ethylene chloride (Faraday), and hence formed in the chlorination of most ethyl compounds in sunlight (Regnault, *A. Ch.* [2] 69, 166; 81, 371; Ebelmen a. Bouquet, *A. Ch.* [3] 17, 66; Malaguti, *A. Ch.* [3] 16, 6, 14; Geuther a. Hofacker, *A.* 108, 51).—3. By passing CCl_4 through a red-hot tube (Kolbe, *A.* 54, 147) or over finely divided copper at 120° (Radziszewski, *B.* 17, 834) or silver at 180° (Goldschmidt, *B.* 14, 928).—4. From AcCl and PCl_5 at 180° (Hubner a. Müller, *Z.* 1870, 328).—5. Ultimate product of the action of PCl_5 on succinic acid.—6. By heating propane, propyl chloride, or isobutyl chloride and ICl_3 at 200° (Krafft a. Merz, *B.* 8, 1298).—7. From propionic acid and ICl_3 (Krafft, *B.* 9, 1085).—8. By chlorination of boiling butyric acid in sunshine (Naumann, *A.* 119, 120).—9. Together with C_6Cl_6 and CCl_4 by heating chrysene with PCl_5 (Ruoff, *B.* 10, 1234).

Properties.—Tables (from alcohol-ether); smells like camphor. Trimorphous, crystallising in the cubic, trimetric, and triclinic systems (Lehmann, *J.* 1882, 369; *Z. K.* 6, 580). Insol. water, sol. alcohol and ether. When its vapour is led through a red-hot tube C_2Cl_4 is formed.

Reactions.—1. Alcoholic *potash* at 100° converts it into oxalic acid (Berthelot, *A.* 109, 118). Solid potash at 200° does the same (Geuther, *A.* 111, 174).—2. Boiling with NaOEt under pressure gives C_2Cl_4, CCl_2:CCl(OEt), $CHCl_2.C(OEt)_3$, and $CH_2(OEt).CO_2Na$ (Geuther a. Brockhoff). Zinc and dilute H_2SO_4 do the same.—3. Finely divided *silver* at 280° also gives C_2Cl_4.—4. SO_3 at 150° forms $CCl_3.COCl$ and $COCl_2$ (Prudhomme, *A.* 156, 342; Armstrong, *Pr.* 18, 502).—5. Al_2I_6 forms C_2Cl_4, Al_2Cl_6, and iodine (Gustavson, *B.* 9, 1607).

CHLORO-ETHANE TRI-CARBOXYLIC ACID.

Ethyl ether $(CO_2Et)_2.CCl.CH_2(CO_2Et)$ (205°–215°) at 160 mm. From ethane tri-carboxylic ether and chlorine (Bischoff, *A.* 214, 46).

Reactions.—1. Boiling aqueous HCl forms fumaric acid.—2. KOH and dilute alcohol form malic acid.—3. KOH and 97 p.c. alcohol appear to form $(CO_2Et)_2.C(OEt).CH_2.CO_2Et$.

α-CHLORO-ETHANE SULPHONIC ACID $CH_3.CHCl.SO_3H$. Its sodium salt A′Na is formed by heating ethylidene chloride with solution of Na_2SO_3 at 140°. This salt forms plates, sol. alcohol (Bunte, *A.* 170, 317).

β-Chloro-ethane sulphonic acid $CH_2Cl.CH_2.SO_3H$.

Formation.—1. By the action of fuming HNO_3 on $CH_2Cl.CH_2.SCy$ (James, *J. pr.* [2] 20, 353).—2. By boiling its chloride with water (Dittrich, *J. pr.* [2] 18, 67; Kolbe, *A.* 122, 33).—3. From $(CH_2Cl.CH_2)_2S_2$ and HNO_3 (Spring a. Lecrenier, *Bl.* [2] 48, 629).

Properties.—Very deliquescent needles. Not decomposed by boiling water. Heated with *ammonia* in sealed tubes at 100° forms taurine, $CH_2(NH_2)CH_2SO_3H$.

Salts.—(R. Hübner, *A.* 223, 213; James, *J. pr.* [2] 26, 382; *C. J.* 43, [illegible]1).—NH_4A'.—$NaA'aq$. KA': needles, insol. alcohol.—BaA'_2 aq (H.).—BaA'_2 2aq: needles (J.).—PbA'_2 2aq.—CuA'_2 3aq (H.).—CuA'_2 4aq: triclinic tablets (J.).—ZnA'_2 4aq (H.).—ZnA'_2 6aq: plates (J.).—MgA'_2 4aq.—SrA'_2 2aq: needles.—MnA'_2 4aq.—FeA'_2 4aq.—$NMeH_3A'$: plates (from alcohol).

Chloride.—$CH_2Cl.CH_2SO_2Cl$ (200°–205°). From potassic isethionate and PCl_5 (Kolbe, *A.* 122, 38). Also from $SO_2Cl.CH_2.CH_2.SO_2Cl$ and PCl_5 (Kõnigs, *B.* 7, 1163). It is one of the products of the action of SO_3 on ethyl chloride (Purgold, *B.* 6, 502). Oil, smelling like mustard. Does not give an amide with ammonia, or an ether when heated with alcohol. PCl_5 at 200° gives ethylene chloride.

Di-chloro-ethane sulphonic acid $C_2H_3Cl_2(SO_3H)$. From ethane sulphonic acid and ICl_3 (Spring a. Winssinger, *B.* 15, 446). Converted by baryta into chloro-isethionic acid $C_2H_3Cl(OH)(SO_3H)$. Ammonia at 100° gives chlorinated taurine.

CHLORO-ETHENYL-TRICARBOXYLIC ACID *v.* Chloro-ethane-tricarboxylic acid.

CHLORO-ETHER *v.* Chloro-ethyl oxide.

CHLORO-ETHULMIC ACID $C_6H_9ClO_2$. A brown amorphous body formed by adding sodium to chloroform containing alcohol (Hardy, *A. Ch.* [3] 65, 340).

CHLORO-ETHYL-ACETAMIDE *v.* Chloro-ethylamine.

ω-CHLORO-ETHYL ACETATE $CH_3.CHCl.OAc$ *v.* Aldehyde.

α-Chloro-ethyl acetate $CH_2Cl.CH_2.OAc$ *v.* Chloro-ethyl alcohol.

Other Chloro-ethyl acetates *v.* Acetyl derivatives of the corresponding chloro-ethyl alcohols.

CHLORO-ETHYL-ACETO-ACETIC ETHER $C_8H_{13}ClO_3$ *i.e.* $CH_2Cl.CO.CHEt.CO_2Et$ (192·5° cor.). S.G. ^{15} 1·052. A product of action of PCl_5 on ethyl-aceto-acetic ether (Isbert, *A.* 234, 187; *cf.* Conrad, *A.* 186, 241). Oil, smelling of peppermint. Sol. alcohol or ether. With dilute HCl at 180° it gives mono-chlorinated methyl propyl ketone. With NaOEt (1 mol.) in alcohol, it gives rise to ethoxy-ethyl-aceto-acetic ether $CH_2(OEt).CO.CHEt.CO_2Et$ (210° cor.). S.G. ^{22} ·957. Alcoholic KOH at 120° converts it into $EtO.CH_2.CO.CH_2Et$.

Di-chloro-ethyl-aceto-acetic ether $C_8H_{12}Cl_2O_3$. (220°–225°). S.G. ^{15} 1·183. Formed at the same time as the preceding.

Chloro-di-ethyl-aceto-acetic ether $CH_2Cl.CO.CEt_2.CO_2Et$. S.G. ^{15} 1·063. PCl_5 has no action on di-ethyl-aceto-acetic ether, even at 100°, but at a higher temperature HCl, EtCl, ethyl-chloro-crotonic (chloro-hexenoic) ether, di-ethyl-chloro-aceto-acetic ether, and di-ethyl-di-chloro-aceto-acetic ethers are formed. The product is freed from PCl_5 by distillation, is then poured into water and distilled with steam (James, *C. J.* 49, 50; *A.* 231, 235). Di-ethyl-chloro-aceto-acetic ether is a liquid, which is converted by treatment with sodium methylate MeONa into $CH_2(OMe).CO.CEt_2.CO_2Et$ and $CH_2(OMe).CO.CHMeEt$ (131°). S.G. ^{20} ·855.

Di-chloro-di-ethyl-aceto-acetic ether $CHCl_2.CO.CEt_2.CO_2Et$. S.G. ^{15} 1·155. One of the products of the action of PCl_5 on di-ethyl-aceto acetic ether. Oil, with pleasant smell. Miscible with alcohol and with ether. Converted by NaOMe into $CH(OMe)_2.CO.CEt_2.CO_2Et$ (c. 195°) and $CH(OMe)_2.CO.CHEt_2$ (134°). S.G. ^{15} ·886 (James, *C. J.* 49, 57).

ω-CHLORO-ETHYL ALCOHOL $CH_3.CHCl.OH$. *Ethylidene chlorhydrin.* (25°) at 40mm. An unstable body formed by combination of aldehyde with HCl in the cold. It changes spontaneously into 'ethylidene oxy-chloride' or di-chloro-di-ethyl oxide (Hanriot, *A. Ch.* [5] 25, 219), *v.* Aldehyde, vol. i. p. 104.

Acetyl derivative $CH_3.CHCl.OAc$. (121·5° cor.). Formed by combination of aldehyde with acetyl chloride; *v.* Aldehyde, vol. i. p. 105, where other alkoyl derivatives are described.

Methyl derivative $CH_3.CHCl.OMe$. (c. 74°). S.G. ^{17} ·996. Formed by passing HCl into a well-cooled mixture of aldehyde (1 vol.) and methyl alcohol ($1\frac{1}{2}$ vols.) (Rübencamp, *A.* 225, 269).

Ethyl derivative $CH_3.CHCl.OEt$ *v.* Chloro-di-ethyl oxide.

Chloro-ethyl alcohol C_2H_5ClO *i.e.* $CH_2Cl\ CH_2OH$. *Glycol chlorhydrin.* Mol. w. $80\frac{1}{2}$ (128°–131°). S.G. ^{0} 1·2233.

Formation.—1. By repeatedly saturating glycol with HCl and distilling the product (Wurtz, *A.* 110, 125; *cf.* Schorlemmer, *C. J.* 39, 143). Besides the pure product (128°) a fraction boiling at 106° is obtained; this fraction may be represented as $(C_2H_5ClO)_2HCl$ 8aq, and has S.G. ^{0} 1·1926; by means of KOH (1 mol.) it may be decomposed with liberation of the pure chlorhydrin (Bouchardat, *C. R.* 100, 452).—2. By heating glycol with S_2Cl_2 at 100° and extracting the product with moist ether (Carius, *A.* 124, 257); the yield is over 50 p.c. of the theoretical.—3. From ethylene and ClOH (Carius, *A.* 126, 197; *cf.* Butlerow, *A.* 144, 40).—4. From ethylene oxide and HCl; the union is attended with disengagement of heat: $(C_2H_4O,HCl) = 36{,}000$ (Berthelot, *C. R.* 93, 185).

Properties.—Liquid, miscible with water. A mixture of glycol chlorhydrin (1 mol.) with water (4 mols.) solidifies at −17°.

Reactions.—1. *Oxidised* by chromic mixture to chloro-acetic acid (Kriwaxin, *Z.* 1871, 265).—2. Reduced by *sodium amalgam* and water to alcohol (Lourenço, *A.* 120, 92).—3. Converted by *potash* into ethylene oxide.—4. With $COCl_2$, in the cold, reacts thus: $CH_2Cl.CH_2OH + Cl_2CO = HCl + CH_2Cl.CH_2.O.COCl$, forming the chloro-ethylic ether of chloro-formic acid.—5. Heated with K_2SO_3 and water at 180° it forms isethionic acid $CH_2OH.CH_2SO_3H$.—6. *Ammonia* forms oxyethyl-amine $CH_2OH.CH_2NH_2$ together with $CH_2OH.CH_2.O.CH_2.CH_2NH_2$ (Wurtz, *A.* 114, 51; 121, 226).—7. *Trimethylamine* in aqueous solution forms neurine (Wurtz, *A. Suppl.* 6, 116, 197).—8. *Dimethylamine* gives di-methyl-oxy-ethyl-amine $CH_2OH.CH_2.NMe_2$ (Ladenburg, *B.* 14, 2408), and $CH_2OH.CH_2.O.CH_2.CH_2NMe_2$ (Morley, *C. J.* 37, 234).

Nitroxyl derivative $CH_2Cl.CH_2.O.NO_2$. *Chloro-ethyl nitrate.* (150°). S.G. ^{21} 1·378. From $CH_2Cl.CH_2OH$, nitric acid, and H_2SO_4, or from $CH_2Cl.CH_2Br$ and alcoholic $AgNO_3$ (*A. Ch.* [4] 27, 257; Henry, *C. R.* 96, 1062). Oil.

Acetyl derivative $CH_2Cl.CH_2OAc$. *Glycol chloracetin.* (145°). S.G. ^{0} 1·1783. *Formation.*—1. From glycol, HOAc, and gaseous HCl at 100°

(Simpson, *A*. 112, 147).—2. From $CH_2OH.CH_2OAc$ and HCl (Simpson, *A*. 113, 116). - 3. From glycol and AcCl in the cold (Lourenço, *A. Ch.* [3] 67, 260, 114, 126).—4. From chloro-ethyl alcohol $CH_2Cl.CH_2OH$ and AcCl (Henry, *B*. 7, 70; Delacre, *Bl*. [2] 48, 707), or Ac_2O at 110° (Ladenburg a. Demole, *B*. 6, 1024). *Properties*.—Liquid; converted by aqueous potash into ethylene oxide.

Chloro-acetyl derivative $CH_2Cl.CH_2.O.CO.CH_2Cl$. (198°). From chloro ethyl alcohol and chloro-acetyl chloride (Delacre, *Bl*. [2] 48, 708), or from ethylene and Cl_2O (Mulder a. Bremer, *B*. 11, 1958).

Di-chloro-acetyl derivative $CH_2Cl.CH_2.O.CO.CHCl_2$. (211°). S.G. $\frac{15}{15}$ 1·200 (D.).

Tri-chloro-acetyl derivative $CH_2Cl.CH_2O.CO.CCl_3$. (217°). S.G. $\frac{15}{15}$ 1·251 (D.).

Butyryl derivative $CH_2Cl.CH_2O.CO.Pr$. (190°). S.G. ^{0} 1·0854. From glycol, butyric acid, and gaseous HCl (Simpson, *A*. 113, 119).

Benzoyl derivative $CH_2Cl.CH_2.OBz$. (260°-270°). From glycol, benzoic acid, and HCl at 100° (S.).

ωα-Di-chloro-ethyl-alcohol $CH_2Cl.CHCl.OH$.

Acetyl derivative $CH_2Cl.CHCl.OAc$. (c. 163°). From acetyl-chloride and the hydrate of chloro-acetic aldehyde (Natterer, *M*. 3, 453). Oil. An isomeride (147°) is formed by treating $CCl_3.CHCl.OAc$ with Zn and HOAc (Curie a. Milliet, *B*. 9, 1611).

Di-chloro-ethyl alcohol $CHCl_2.CH_2.OH$. (146° i.V.). S.G. $\frac{15}{15}$ 1·145. V.D. 3·93 (calc. 3·97) (Delacre, *C. R.* 104, 1184). From di-chloro-acetic aldehyde and $ZnEt_2$, the product being decomposed by water. Liquid, sl. sol. water, sol. alcohol and ether. Reduces ammoniacal $AgNO_3$. Does not dissolve $CaCl_2$. Fuming HNO_3 gives di-chloro-acetic acid. Converted by PCl_5 into $CHCl_2.CH_2Cl$ (115°), and by PBr_3 into $CHCl_2.CH_2Br$ (138°).

Nitroxyl derivative $CHCl_2.CH_2.NO_3$. *Di-chloro-ethyl nitrate*. (156° i.V.). V.D. 5·56 (calc. 5·53) (De Lacre, *C. R.* 104, 1186). From $CHCl_2.CH_2OH$ by HNO_3 and H_2SO_4.

Acetyl derivative $CHCl_2.CH_2.OAc$. *Di-chloro-ethyl acetate*. (167° i.V.). V.D. 5·74 (calc. 5·42). S.G. $\frac{15}{15}$ 1·104 (Delacre, *C. R.* 104, 1186).

Chloro-acetyl derivative $Cl_2CH.CH_2O_2C.CH_2Cl$. (215° cor.). S.G. $\frac{15}{15}$ 1·216. Prepared by acting with mono-chloro-acetyl chloride on di-chloro-ethyl alcohol on the water-bath until no more hydric chloride is evolved (Delacre, *Bl*. [2] 48, 708).

Di-chloro-acetyl derivative $Cl_2CH.CH_2O_2C.CHCl_2$. (223°). S.G. $\frac{15}{15}$ 1·25. Formed by heating di-chloro-ethyl alcohol and di-chloro-acetyl-chloride together on the water-bath (Delacre).

Tri-chloro-acetyl derivative $Cl_2CH.CH_2O_2C.CCl_3$. (230°). Formed by the action of tri-chloro-acetyl chloride on di-chloro-ethyl alcohol (Delacre).

Tri-chloro-ethyl alcohol $CCl_3.CH_2OH$. [18°]. (151°). S.G. $\frac{28}{28}$ 1·550.

The zinc salt $(CCl_3.CH_2.O)_2Zn$ is formed by the action of $ZnEt_2$ on chloral; it is decomposed by water into $Zn(OH)_2$ and tri-α-chloro-ethyl alcohol (Garzarolli-Thurnlackh, *A*. 210, 63; Delacre, *Bl*. [2] 48, 785). It is also formed, together with glycuronic acid $C_6H_{10}O_7$, by treating urochloralic acid with dilute HCl (Kulz, *Z. B.* 20, 161). Hygroscopic trimetric tables; sl. sol. water, v. sol. alcohol and ether. HNO_3 forms tri-chloro-acetic acid. Reduces hot Fehling's solution.

Acetyl derivative $Cl_3C.CH_2OAc$. (170°). S.G. $\frac{15}{15}$ 1·189. Formed by digesting at a gentle heat acetyl chloride and trichloro-ethyl alcohol.

Chloro-acetyl derivative $Cl_3C.CH_2O_2C.CH_2Cl$. (220° cor.). S.G. $\frac{15}{15}$ 1·25. From chloro-acetyl-chloride and tri-chloro-ethyl alcohol (Delacre, *Bl*. [2] 48, 710).

Di-chloro-acetyl derivative $Cl_3C.CH_2O_2C.CHCl_2$. (231°) at 767 mm. S.G. $\frac{15}{15}$ 1·267. From di-chloro-acetyl chloride and tri-chloro-ethyl alcohol.

Tri-chloro-acetyl derivative $Cl_3C.CH_2O_2C.CCl_3$. [26°]. (236°). From tri-chloro-acetyl chloride and tri-chloro-ethyl alcohol.

ωαα-Tri-chloro-ethyl alcohol. *Acetyl derivative* $CHCl_2.CHCl.OAc$. (185°). From AcCl and di-chloro-acetic aldehyde (Delacre, *Bl*. [2] 48, 714).

DI-CHLORO-ETHYLAMIDO-ACETIC ETHER $C_6H_{11}Cl_2NO_2$ *i.e.* $NHEt.CCl_2.CO_2Et$. [above 50°]. From $NHEt.CO.CO_2Et$ and PCl_5 (Wallach, *A*. 184, 76). Needles or prisms. Water regenerates $NHEt.CO.CO_2Et$. Ammonia forms ethyl-oxamide.

***p*-CHLORO-TETRA-ETHYL-*p*-DI-AMIDO-TRI-PHENYL-CARBINOL** $C_6H_4Cl.C(OH):(C_6H_4.NEt_2)_2$. [121°]. Large glistening colourless tables. Formed by oxidation of its leuco-base, the condensation-product of diethylaniline and *p*-chlorobenzaldehyde. Its zinc double chloride is a bluish-green dyestuff (Kaeswurm, *B*. 19, 745).

TRI-CHLORO-*p*-ETHYL-AMIDO-PHENYL-ETHYL ALCOHOL $CCl_3.CH(OH).C_6H_4.NHEt$. [98°]. From chloral hydrate and ethyl-aniline. Crystals (from alcohol). B'HCl.

Nitrosamine $CCl_3.CH(OH).C_6H_4.NEt.NO$ [138°]. Crystals (Boessneck, *B*. 21, 783).

Tri-chloro-di-ethyl-amido-phenyl ethyl alcohol $CCl_3.CH(OH).C_6H_4.NEt_2$. Yellow oil. Formed by adding 10 grms. of $ZnCl_2$ to a cold mixture of 60 grms. of diethylaniline and 20 grms. of chloral hydrate, and allowing to stand for 2 days at 40°. It is decomposed by alkalis into chloroform and *p*-di-ethyl-amido-benzaldehyde. — B'HCl: crystalline solid (Boessneck, *B*. 19, 367).

***p*-CHLORO-TETRA-ETHYL-*p*-DI-AMIDO-TRI-PHENYL-METHANE** $C_6H_4Cl.CH(C_6H_4.NEt_2)_2$. [110°]. Obtained by heating together di-ethyl-aniline, *p*-chloro-benzaldehyde, and $ZnCl_2$ (Kaeswurm, *B*. 19, 744). Small colourless needles. Sol. benzene, alcohol, and ether, insol. water. On oxidation it gives a bluish-green dyestuff.

CHLORO-ETHYL-AMINE *v. Ethyl-chloro-amine*, described under ETHYL-AMINE.

β-Chloro-ethyl-amine $Cl.CH_2.CH_2.NH_2$. From vinylamine and conc. HClAq. Formed also by heating oxyethylphthalimide with conc. HCl to 200° (Gabriel, *B*. 21, 573, 1049).—**Salts.**—B'HCl. V. e. sol. alcohol, ether, and water.—**Picrate.**—$B'C_6H_3N_3O_7$ $\frac{1}{2}$aq. Yellow needles. [143° anhydrous]. $B'_2H_2PtCl_6$. Orange plates. V. sol. water, sl. sol. alcohol.

CHLORO-ETHYL-ANILINE $C_8H_{10}ClN$ *i.e.* $C_6H_5.NH.CH_2.CH_2Cl$. Formed by the action of fuming HCl at 170° on the compound $C_9H_9NO_2$ derived from phenyl-carbamic acid (*q. v.*).—B′HCl. [158°] (Nemirowsky, *J. pr.* [2] 31, 175).

p-**Chloro-ethyl-aniline** [4:1] $C_6H_4Cl.NHEt$. From *p*-chloro-aniline and EtBr. Liquid (Hofmann, *A.* 74, 143).

p-**Chloro-di-ethyl-aniline** [4:1] $C_6H_4Cl.NEt_2$. From the preceding and HBr (H.). Liquid.—$B'_2H_2PtCl_6$.

Eso-**CHLORO-ETHYL-BENZENES** $C_6H_4Cl.(C_2H_5)$. The three eso-chloro-ethyl-benzenes are obtained simultaneously by the action of C_2H_4 upon C_6H_5Cl (500 g.), in presence of Al_2Cl_6 (100 gr.). The mixture is an oily liquid (c. 180°). S.G. ^{0} 1·068. V.D. 4·77. Very volatile, and of agreeable odour. Sol. ligroin (1 vol.), CS_2, $CHCl_3$, and ether. Sol. C_6H_6 (2 vols.) and alcohol (3 vols.). The proportion of the three isomerides is roughly $o:m:p = 7:10:3$. On oxidation it gives a mixture of the three chloro-benzoic acids. Heated with sulphuric acid it gives sulphonic acids (Istrati, *A. Ch.* [6] 6, 402; *Bl.* [2] 42, 114).

ω-**Chloro-ethyl-benzene** $CH_2Cl.CH_2.C_6H_5$ (?). (c. 202°). Formed by chlorinating boiling ethyl-benzene (Fittig a. Kiesow, *A.* 156, 246; *cf.* Schramm, *M.* 8, 105). Split up by boiling into HCl and styrene. Converted by alcoholic KCy into the nitrile of *β*-phenyl-propionic acid (?).

α-**Chloro-ethyl-benzene** $CH_3.CHCl.C_6H_5$. (194°). Formed by the action of chlorine on ethyl-benzene in sunlight, and also on boiling ethyl-benzene (Schramm, *M.* 8, 101). Formed also by passing HCl into cold *ω*-phenyl-ethyl alcohol $C_6H_5.CH(OH).CH_3$ (Engler a. Bethge, *B.* 7, 1127). With benzene and Al_2Cl_6 it gives *s*-di-phenyl-ethane (Anschütz, *A.* 235, 329).

Chloro-di-ethyl-benzenes $C_6H_3Cl(C_2H_5)_2$. A mixture of chloro-di-ethyl-benzenes is formed by treating C_6H_5Cl with C_2H_4 in presence of Al_2Cl_6. It is a mobile liquid, with agreeable odour. (c. 218°). S.G. ^{0} 1·036. V.D. 5·65. Sol. ligroïn (in all proportions), CS_2, ether, and $CHCl_3$. Sol. benzene (3 vols.), alcohol (7 vols.). On oxidation, it gives rise to two chloro-phthalic acids, and chloro-ethylphenyl methyl ketone $(C_2H_5).C_6H_3.Cl.CO.CH_3$ (Istrati).

Chloro-tri-ethyl-benzenes $C_6H_2Cl(C_2H_5)_3$. A mixture of these substances is obtained by continuing the passage of ethylene into chloro-benzene in presence of Al_2Cl_6. Mobile liquid. (248°). V.D. 6·87. Sol. (in all proportions) ether, petroleum ether, CS_2, and $CHCl_3$. Sol. benzene (3½ vols.), and alcohol (30 vols.). On oxidation with permanganate it gives a tri-carboxylic acid, having an insol. Ba salt (Istrati, *A. Ch.* [6] 6, 426).

Chloro-tetra-ethyl-benzenes $C_6HCl(C_2H_5)_4$. A mixture of isomerides of this composition is formed by the further action of C_2H_4 upon C_6H_5Cl in presence of Al_2Cl_6. Liquid. S.G. ^{0} 1·022. (c. 271). V.D. 7·17. V. sol. ether, ligroin, CS_2, and $CHCl_3$. Sol. benzene (4 vols.) and 90 p.c. alcohol (26 vols.) (Istrati).

Chloro-penta-ethyl-benzene $C_6Cl(C_2H_5)_4$. Formed by the prolonged action of C_2H_4 upon C_6H_5Cl in presence of Al_2Cl_6. The yield is not good. Mobile liquid. S.G. ^{0} 1·065. (c. 292°). V.D. 8·48. V. sol. ether, ligroïn, CS_2, and $CHCl_3$. Sol benzene (5½ vols.) and 90 p.c. alcohol (32 vols.) (Istrati, *A. Ch.* [6] 6, 128).

Di-chloro-ethyl-benzene $C_6H_3Cl_2(C_2H_5)$ [1:4:2]. S.G. ^{0} 1·239 (213°) V.D. 6·24 Formed by the action of C_2H_4 upon $C_6H_4Cl_2$ [1:4] in presence of Al_2Cl_6, at 125°-150° (Istrati, *A. Ch.* [6] 6, 476). Liquid. Sol. benzene (3 vols.) and 90 p.c. alcohol (9 vols.). Yields a di-chloro-benzoic acid on oxidation.

ωω-**Di-chloro-ethyl-benzene** $C_6H_5.CH_2.CCl_2H$. *Phenyl-di-chloro-ethane* Formed by the action of PCl_5 on phenyl-acetic aldehyde (Forrer, *B.* 17, 982). Heavy colourless liquid. Volatile with steam. By boiling with water it is converted into *ω*-chloro-styrene.

αα-**Di-chloro-di-ethyl-benzene** $C_6H_5.CCl_2.CH_3$. *Acetophenone chloride.* From acetophenone and PCl_5 in the cold (Friedel, *Bl.* 1, 7; Ladenburg, *A.* 217, 105). Readily splits off HCl.

ωα-**Di-chloro-di-ethyl-benzene** $C_6H_5.CHCl.CH_2Cl$. *Styrene dichloride.* From styrene and chlorine (Blyth a. Hofmann, *A.* 53, 309). Decomposed on distillation. Alcoholic KOH gives $C_6H_5.CH:CHCl$.

Di-chloro-di-ethyl-benzene $C_6H_2Cl_2(C_2H_5)_2$. A mixture of di-chloro-di-ethyl-benzenes is obtained by treating *p*-di-chlor-benzene with C_2H_4 in presence of Al_2Cl_6. Liquid. S.G. ^{0} 1·179. (c. 247°). V.D. 7·17. Sol. benzene (4 vols.) and alcohol (16 vols.) (Istrati, *A. Ch.* [6] 6, 482).

Di-chlor-tri-ethyl-benzene $C_6HCl_2(C_2H_5)_3$ [1:4:3:5:6]. S.G. ^{0} 1·131. (c. 273°). V.D. 8·77 (calc. 7·99). Formed by the action of C_2H_4 upon *p*-di-chlor-benzene in presence of Al_2Cl_6 (Istrati). Liquid. Sol. benzene (5 vols.), alcohol (30 vols.). HNO_3 gives $C_6(NO_2)Cl_2(C_2H_5)_3$. [20°]. (312°). H_2SO_4 gives $C_6(SO_3H)Cl_2.(C_2H_5)_3$.

Di-chloro-tetra-ethyl-benzene $C_6Cl_2(C_2H_5)_4$ S.G. ^{0} 1·129. (296°). V.D. 9·26 (calc. 8·96). Prepared by the action of C_2H_4 upon *p*-di-chloro-benzene in presence of Al_2Cl_6. Liquid. Sol. 90 p.c. alcohol (46 vols.) and benzene (6 vols.) (Istrati, *A. Ch.* [6] 6, 485).

Tri-chloro-ethyl-benzene $C_6H_2Cl_3(C_2H_5)$. A mixture of these bodies is formed by treating $C_6H_3Cl_3$ [1:2:4] with C_2H_4 in presence of Al_2Cl_6 (Istrati, *A. Ch.* [6] 6, 490). Liquid. S.G. ^{0} 1·389. (214°). V.D. 7·24. Sol. benzene (3½ vols.) and alcohol (17 vols.).

Tri-chloro-di-ethyl-benzene $C_6HCl_3(C_2H_5)_2$. A mixture of these bodies is obtained by treating $C_6H_3Cl_3$ [1:2:4] with C_2H_4 in presence of Al_2Cl_6. Liquid, greases paper. S.G. ^{0} 1·305. (269°). V.D. 8·37. Sol. benzene (5 vols.) and alcohol (26 vols.).

Tri-chloro-tri-ethyl-benzene $C_6Cl_3(C_2H_5)_3$. S.G. ^{0} 1·240. (291°). V.D. 8·42 (calc. 8·19). Prepared by passing C_2H_4 into a mixture of Al_2Cl_6 and $C_6H_3Cl_3$ [1:2:4]. Oil. Sol. benzene (5 vols.) and alcohol (41 vols.).

Tetra-chloro-ethyl-benzene $C_6HCl_4(C_2H_5)$. S.G. ^{0} 1·543. (c. 272°). V.D. 7·99 (calc. 8·47). Formed by treating $C_6H_2Cl_4$ [1:3:4:5] with C_2H_4 in presence of Al_2Cl_6. Yellowish liquid. Sol. benzene (5½ vols.) and 90 p.c. alcohol (16 vols.). HNO_3 gives a nitro-derivative [30°] (Istrati, *A. Ch.* [6] 6, 497).

ααωω-**Tetra-chloro-ethyl-benzene** $CHCl_2.CCl_2.C_6H_5$. From di-chloro-styrene and Cl (Dyckerhoff, *B.* 10, 533). Liquid. On distillation it splits up into HCl and $CCl_2:CCl.C_6H_5$.

Tetra-chloro-di-ethyl-benzene $C_6Cl_4(C_2H_5)_2$ [1:3:4:5:2:6]. S.G. ^{15} 1·431. [45°]. (290°). V.D. 8·44 (calc. 9·07). Formed by treating *u*-tetra-chloro-benzene with ethylene and Al_2Cl_6. Prisms (from a mixture of alcohol and benzene). Sol. benzene (7 vols.) and 90 p.c. alcohol (40 vols.) (Istrati, *A. Ch.* [6] 6, 500).

Penta-chloro-ethyl-benzene $C_6Cl_5(C_2H_5)$. [85°]. (c. 297°). S.G. ^{12} 1·720. V.D. 9·57 (calc. 9·29). Prepared by submitting C_6HCl_5, in presence of C_2H_4, to the influence of Al_2Cl_6. The yield is small. HCl gas facilitates the reaction and gives a better yield. White crystals (from alcohol with benzene). V. sol. ether, $CHCl_3$, ligroin and CS_2. Sol. benzene (9 vols.) and 90 p.c. alcohol (108 vols.). On oxidation with permanganate it gives $C_6Cl_5.CO_2H$, which immediately loses CO_2 forming C_6HCl_5 (Istrati, *A. Ch.* [6] 6, 502).

CHLORO-ETHYL-BENZENE SULPHONIC ACID $C_6H_3Cl(C_2H_5).(SO_3H)$. Formed by heating the mixture of chloro-ethyl-benzenes with H_2SO_4 at 180°. The product appears to consist of several isomerides (Istrati, *A. Ch.* [6] 6, 411).

Eso-**CHLORO-ETHYL-BENZOIC ACID** $C_6H_3(C_2H_5)Cl.CO_2H$. [115°]. Formed by fusing the ketone $C_6H_3Cl.(C_2H_5).CO.CH_3$ with KOH. White solid; insol. water; begins to sublime at 100°.—BaA'_2: small crystals; insol. cold water (Istrati, *A. Ch.* [6] 6, 424).

CHLORO-ETHYL CARBAMATE $NH_2CO_2C_2H_4Cl$. [115°] (G.); [76°] (N.). Formed by the action of chloro-ethyl-alcohol (glycol chlorhydrin) on chloro-formamide (Gattermann, *A.* 244, 41); and of $ClCH_2.CH_2.O.COCl$ on ammonia (Nemirowsky, *J. pr.* [2] 31, 174). Colourless, strongly refractive plates. Insol. cold, m. sol. hot water.

TETRA-CHLORO-DI-ETHYL CARBONATE $(C_2H_3Cl_2)_2CO_3$. Obtained by passing chlorine into carbonic ether in diffused daylight, ultimately at 80° (Cahours, *A. Ch.* [3] 9, 201). Heavy oil, decomposed by heat.

Per-chloro-di-ethyl carbonate $(C_2Cl_5)_2CO_3$. [86°]. Formed by chlorinating the preceding in direct sunshine (Malaguti, *A. Ch.* [3] 16, 30). Mass of needles. Distils with partial decomposition into CO_2, C_2Cl_6, and $CCl_3.COCl$. Solution in alcohol converts it into carbonic and tri-chloro-acetic ethers. Aqueous KOH gives potassium formate, carbonate, and chloride. Gaseous or aqueous ammonia forms tri-chloro-acetamide (Gerhardt, *Traité*, 1, 166) and a substance melting at 37°.

CHLORO-ETHYL-CROTONIC ACID $C_6H_9ClO_2$. *Chloro-hexenoic acid.* [49·5°]. (215°). S. ·2 at 1°; ·33 at 12°. Formed, together with chloro- and di-chloro-ethyl-aceto-acetic ether by the action of PCl_5 upon ethyl-aceto-acetic ether. Needles (from alcohol or ether). Unpleasant, pungent odour (Isbert, *A.* 234, 183; *cf.* Demarçay, *B.* 10, 1177). Not reduced by sodium amalgam.

Salts. — NaA′ deliquescent. — BaA'_2. — CaA'_2 2aq. S. 12 at 19°. Prisms.—AgA′.

Ethyl ether EtA′. (185°).

CHLORO-ETHYL CYANIDE *v.* *Nitrile of* CHLORO-PROPIONIC ACID.

CHLORO-ETHYLENE C_2H_3Cl *i.e.* $CH_2:CHCl$. *Vinyl chloride.* (−16°). V.D. 2·17. H.F.p. −1880 (*Th.*). H.F.v. −2460. Formed by the action of alcoholic KOH on ethylene chloride $CH_2Cl.CH_2Cl$ (Regnault, *A.* 14, 28), or on ethylidene chloride $CH_3.CHCl_2$ (Wurtz a. Frapolli, *A.* 108, 224). It is a gas which polymerises in sunshine, changing to an amorphous mass, S.G. 1·41, which melts and turns black at 130° (Baumann, *A.* 163, 317). Ammonia has no action on chloro-ethylene below 100°, but at 160° it forms ethylene diamine $CH_2NH_2.CH_2NH_2$ (118°) (Engel, *Bl.* [2] 48, 94). Chlorine unites with $CH_2:CHCl$ in sunshine.

u-**Di-chloro-ethylene** $CH_2:CCl_2$. (36°). S.G. ^{15} 1·250. V.D. 3·32 (calc. 3·36). Formed by the action of alcoholic KOH on $CH_2Cl.CHCl_2$ (Regnault, *J. pr.* 18, 80; Krämer, *B.* 3, 261), on $CH_2Br.CHCl_2$, or on di-chloro-iodo-ethane (Henry, *C. R.* 97, 1491; 98, 518). Liquid, with alliaceous odour; changes spontaneously into a crystalline isomeride. Chlorine in daylight followed by sunshine gives C_2Cl_6; direct sunshine gives C and HCl. Does not react with KI.

s-**Di-chloro-ethylene** CHCl:CHCl. *Acetylene dichloride.* Mol. w. 97. (55°). Formed by passing acetylene into cool $SbCl_5$, the resulting crystalline compound $C_2H_2SbCl_5$ being decomposed by water (Berthelot a. Jungfleisch, *A. Ch.* [4] 26, 472; but *cf.* Sabanejeff, *A.* 216, 262). From CHClBr.CHClBr and zinc in alcoholic solution (S.).

Tri-chloro-ethylene $CHCl:CCl_2$. (88°). From either tetra-chloro-ethane by treatment with alcoholic KOH (Berthelot a. Jungfleisch, *C. R.* 79, 542; *A. Suppl.* 7, 255). From C_2Cl_6, zinc, and dilute H_2SO_4 (E. Fischer, *Z.* 1864, 268). Also from chloral and P_2S_5 at 170° (Paternò a. Oglialoro, *B.* 7, 81). With alcoholic KOH it gives $C_2HCl_2.OEt$. Aqueous or alcoholic NH_3 forms $C_2H_2Cl_2$ (37°) (Engel, *C. R.* 104, 1621). Sodium forms acetylene, ethylene, $C_2H_2Cl_2$, and hydrogen (Brunner a. Brandenburg, *B.* 10, 1496; 11, 61).

Tetra-chloro-ethylene C_2Cl_4 *i.e.* $CCl_2:CCl_2$. (121°) (S.); (125°) (C.). S.G. $\frac{24}{4}$ 1·6312 (Schiff, *A.* 220, 97); $\frac{20}{4}$ 1·6190. V.D. 5·82 (calc. 5·75). C.E. (9·4° to 120°) ·001147. μ_β 1·515. R_∞ 49·66 (Bruhl). S.V. 114·18. H.F.p. −1150 (*Th.*). H.F.v. −1730. Discovered by Faraday (*T.* 1821, 47) by subjecting C_2Cl_6 to a red heat either alone or in presence of H. Formed also by treating C_2Cl_6 with alcoholic KHS (Regnault, *A. Ch.* [2] 70, 104; 81, 372), with water and granulated zinc (Geuther, *A.* 107, 212), with alcohol and zinc filings, or with aniline (Bourgoin, *Bl.* [2] 23, 344). Formed also by the action of Al_2Cl_6 on chloral (Combes, *A. Ch.* [6] 12, 298). Obtained, together with CCl_4, by heating per-chloro-propane at 300° (Krafft a. Merz, *B.* 8, 1300).

Reactions.—1. *Bromine* forms in sunshine crystals of $C_2Cl_4Br_2$.—2. Dry *chlorine* combines in sunshine forming C_2Cl_6.—3. *Chlorine-water* gives tri-chloro-acetic acid (Kolbe, *A.* 54, 181).—4. Dry *oxygen* has no action even at 120° (Demole a. Dürr, *B.* 11, 1302).—5. *Potash-fusion* gives potassium oxalate and hydrogen (Geuther, *A.* 111, 174).—6. NaOEt at 120° gives $CHCl_2.C(OEt)_3$, $CHCl_2.CO_2Et$, $CH(OEt)_2.CO_2Na$, and $CCl_2:CCl.OEt$ (Geuther, *J.* 1864, 316; *J. pr.* [2] 7, 108).—7. SO_3 at 150° gives $CCl_3.COCl$.

CHLORO-ETHYLENE OXIDE $C_2H_3Cl.O$. (89°–92°). Formed by heating chloro-iodo-ethylene CHCl:CHI, with water (50 vols.) at 150° for

6 days (Sabanejeff, *A.* '16, 268). Liquid. Sl. sol. water.

CHLORO-ETHYLENE CHLORIDE *v.* Tri-chloro-ethane.

CHLORO-ETHYL ETHER *v.* Chloro-di-ethyl oxide.

TRI-CHLORO-ETHYLIDENE-ACETO-ACETIC ETHER *v.* Aceto-acetic acid.

TRI-CHLORO-ETHYLIDENE DIAMINE.

Acetyl derivative $CCl_3.CH(NHAc)_2$. Formed by heating chloral with aceto-nitrile (Hübner, *Z.* 1871, 712; Hepp, *B.* 10, 1651), the equation being: $CCl_3.CHO + 2CH_3CN + H_2O = CCl_3.CH(NH.CO.CH_3)_2$. Needles (from glacial acetic acid). Sol. water and alcohol. Sublimes without melting.

Benzoyl derivative $CCl_3.CH(NHBz)_2$. [257°]. From chloral, benzonitrile, and conc. H_2SO_4. Needles; v. sl. sol. ether.

CHLORO-ETHYLIDENE-ANILINE C_8H_8NCl *i.e.* $CH_2Cl.CH{:}NC_6H_5$. [136°].

Preparation.—Di-chloro-di-ethyl oxide $CH_2Cl.CHCl.OEt$ (1 mol.) is warmed with aniline (2 mols.) in the presence of water. A white powder [87°] is formed, which becomes red [136°] when dried.

Properties.—Red brown powder. Sol. alcohol; it may be a polymeride of the white compound.

Reactions.—1. HNO_2 produces a yellowish grey amorphous body which gives a blue colour with phenol and conc. H_2SO_4.—2. Warmed with aniline it forms phenylamido-ethylidene aniline $C_6H_5N{:}CH.CH_2.NHC_6H_5$ [104°] which yields indole on heating (Berlinerblau a. Polikiev, *M.* 8, 187–189).

CHLORO-ETHYLIDENE DI-CARBAMIC ETHER $C_8H_{15}ClN_2O_4$ *i.e.* $CH_2Cl.CH(NH.CO_2Et)_2$. [147°]. Formed by the action of chlorine on a strong solution of HCN in alcohol; and also by adding conc. aqueous HCl to a solution of carbamic ether in chloro-acetal $CH_2Cl.CH(OEt)_2$ (Bischoff, *B.* 5, 81; 7, 630). Formed also by chlorinating ethylidene di-carbamic ether (Schmid, *J. pr.* [2] 24, 122). Needles (from dilute alcohol). V. sol. ether and alcohol.

Di-chloro-ethylidene di-carbamic ether $CHCl_2.CH(NH.CO_2Et)_2$. [122°]. Formed by passing Cl into an alcoholic solution of $HgCy_2$ (Stenhouse, *A.* 33, 92; Bischoff, *B.* 5, 82). Also by passing chlorine into carbamic ether at 90° (Schmid, *J. pr.* [2] 24, 120). Long needles; v. sol. alcohol and ether.

TRI-CHLORO-ETHYLIDENE-TRI-CHLORO-LACTATE *v.* Chloralide.

CHLORO-ETHYLIDENE GLYCOL, *derivatives of, v.* Chloro-aldehyde.

TRI-CHLORO-ETHYLIDENE-MALONIC ACID $CCl_3.CH{:}C(CO_2H)_2$.

Ethyl ether Et_2A''. (160°–164°) at 23 mm. From chloral, malonic ether and Ac_2O at 160° (C. M. Thompson, *A.* 218, 169).

TRI-CHLORO-ETHYLIDENE-DI-PHENYL-DIAMINE *v.* Tri-chloro-di-phenyl-ethylidene-diamine.

TRI-CHLORO-ETHYLIDENE-QUINALDINE *v.* (*Py.* 3)-Quinolyl-acrylo-tri-chloride.

CHLORO-ETHYLIDENE-*p*-TOLUIDINE $C_9H_{10}NCl$ *i.e.* $CH_3.C_6H_4.N.CH.CH_2Cl$. [58°]. Prepared by decomposing di-chloro-ether $CH_2Cl.CHCl.OEt$ with water, and adding *p*-toluidine. Sol. alcohol and ether; forms with aniline or toluidine a compound free from chlorine. Heated with aniline it yields indole (Berlinerblau a. Polikiev, *M.* 8, 190, 191).

DI-CHLORO-ETHYLIDENE-UREA $CO(NH)_2CH.CHCl_2$. From di-chloro-acetic aldehyde and urea (Schiff, *A.* 151, 186). Needles.

Tri-chloro-ethylidene-di-urea $C_4H_7Cl_3N_4O_2$ *i.e.* $CCl_3.CH(NH.CO.NH_2)_2$. Is the chief product of the reaction of chloral-cyanhydrin with urea. White needles. Insol. ordinary solvents (Pinner a Lifschütz, *B.* 20, 2346).

CHLORO-ETHYL-MALONIC ETHER $C_2H_5.CCl.(CO_2Et)_2$. (228°). S.G. $\frac{17}{}$ 1·11. Liquid Prepared by passing Cl into ethyl-malonic ether (Conrad, *B.* 14, 618). By saponification with baryta-water it gives ethyl-tartronic acid.

DI-CHLORO-ETHYL MERCAPTAN $CH_2Cl.CH_2.SCl$(?). S.G. $\frac{13}{}$ 1·408. Said to be formed from ethylene and SCl_2 (Guthrie, *A.* 113, 275). Pungent oil, sl. sol. ether.

CHLORO-DI-ETHYL OXIDE C_4H_9ClO *i.e.* $CH_3.CHCl.OEt$. *Aldehyde ethylo-chloride.* Mol. w. 108½. (98°).

Formation.—1. The first product of the action of chlorine on ether (Lieben, *A.* 111, 121; 146, 180; Abeljanz, *A.* 164, 197; Jacobsen, *B.* 4, 215).—2. By the action of HCl on an alcoholic solution of aldehyde (Wurtz a. Frapolli, *A.* 108, 226; Claus a. Trainer, *B.* 19, 3001).—3. By the action of PCl_5 (1 mol.) on di-ethyl-acetal (1 mol.) (Bachmann, *A.* 218, 39).—4. By the union of aldehyde with EtCl.

Reactions.—1. NaOEt gives acetal.—2. Conc. H_2SO_4 gives $EtHSO_4$, aldehyde and HCl.—3. Cold *water* forms aldehyde, alcohol, and HCl. Water at 80° gives aldehyde (Laatsch, *A.* 218, 36). *Alkalis* act in the same way. Cold *alcohol* has no action, but at 80° aldehyde and EtCl are formed.—4. Decomposes on keeping into HCl and a liquid boiling at 76°.

ω-Chloro-di-ethyl oxide $CH_2Cl.CH_2.OEt$. (108°). S.G. $\frac{0}{}$ 1·0572. V.D. 3·73 (calc. 3·74). From iodo-di-ethyl oxide by the action of Cl, of $SbCl_5$, or of ICl in presence of water (Henry, *C.R.* 100, 1007). It is not affected by light or by water.

ωα-Di-chloro-di-ethyl oxide $CH_2Cl.CHCl.OEt$. (c. 143°). S.G. $\frac{23}{}$ 1·174. V.D. 4·93. Obtained by the action of chlorine on ether below 30° (Lieben, *A.* 111, 121; 123, 130; 133, 287; 141, 236; 146, 180; 150, 87; Abeljanz, *A.* 164, 197; *cf.* D'Arcet, *A.* 28, 82; Regnault, *A. Ch.* [2] 71, 392; Malaguti, *A. Ch.* [2] 70, 338; [3] 16, 5, 19). Formed also, together with the preceding, by passing HCl into a mixture of aldehyde and alcohol (Natterer, *M.* 5, 496). Also from vinyl-ethyl oxide $CH_2{:}CH.O.Et$ and Cl.

Reactions.—1. *Water* at 120° gives the compound $CH_2Cl.CH(OH)(OEt)$, together with chloro-acetic aldehyde, glycollic aldehyde, alcohol and HCl.—2. Conc. H_2SO_4 produces $EtHSO_4$, chloro-acetic aldehyde, and HCl.—3. With conc. *potash* it forms chloro-aldehyde alcoholate and its anhydride, and also 'oxychloro-ether,' $CH_2OH.CH_2Cl.OEt$ (151°–155°). This latter body is split up by conc. H_2SO_4 into HCl, alcohol and glycollic aldehyde (?), $CH_2OH.CHO$.—4. NaOEt gives chloro-acetal $CH_2Cl.CH(OEt)_2$ and $CH_2(OEt).CH(OEt)_2$.—5. AgOAc gives $CH_2Cl.CH(OEt)(OAc)$ (Bauer, *A.* 134, 176).—

6. Dry metallic *zinc* acts vigorously, producing HCl, $ZnCl_2$, EtCl, alcohol, $CH_2Cl.CHO$, and a condensation product of the alcoholate of the latter, $C_8H_{16}Cl_2O_3$ (Wislicenus, *A.* 226, 271). —7. *Zinc in presence of water* produces aldehyde, Et_2O, alcohol and chloro-aldehyde, besides small quantities of crotonic-aldehyde, chloro-acetal, β-oxy-chloro-ether ($CH_2OH.CHCl.OEt$) and $(CH_2Cl.CH(OEt))_2O$ (W.).—8. In ethereal solution with $ZnEt_2$ it forms $CH_2Cl.CHEt.OEt$, 'ethyl chloro-ether' (ethyl chloro-butyl oxide). 9. Excess of $ZnEt_2$ gives ethyl hexyl-ether, $CH_2Et.CHEt.OEt$.—10. With $ZnMe_2$ it gives $CH_2Cl.CHMe.OEt$, *i.e.* ethyl chloro-isopropyl ether. -11. Di-chloro-di-ethyl oxide (25 g.) heated with *aniline* (50 g.) and water forms indole (Berlinerblau, *M.* 8, 180).—12. *Phenol* forms $C_2H_3(C_6H_4OH)_3$ (Wislicenus a. Reinhardt, *A.* 243, 151).—13. (α)-*Naphthol* forms amorphous $C_2H_3(C_{10}H_6OH)_3$. (β)-naphthol gives crystalline plates of $C_{22}H_{18}ClO$ [174°] (Wislicenus a. Zwanziger, *A.* 243, 165).—14. *Resorcin*, *Pyrocatechin*, and *Hydroquinone* form compounds of the form $C_2H_3(C_6H_3O_2H_2)_3$ (Wislicenus a. Siegfried, *A.* 243, 171).—15. *Thiourea* forms thiazoline (Hantsch a. Traumann, *B.* 21, 938).

Di-chloro-di-ethyl oxide $(CH_3.CHCl)_2O$. *Ethylidene oxychloride.* (117°). S.G. $^{14\cdot5}$ 1·136. V.D. 5·08 (calc. 4·95). From dry aldehyde cooled by a freezing mixture by passing dry HCl into it. The product is dried with $CaCl_2$ and distilled (Lieben, *C. R.* 46, 662; Kessel, *A.* 175, 44; 176, 44; Geuther, *A.* 218, 16).

Reactions.—1. *Water* on warming decomposes it into HCl and aldehyde. -2. *Alcohol* forms chloro-diethyl oxide $(CH_3.CHCl)_2O + 2HOEt = 2CH_3.CHCl(OEt) + H_2O$. -3. NaOEt converts it (in ethereal solution) into aldehyde-resin, acetal, and alcohol —4. Alcoholic *sodium ethylate* forms, besides the same products, a liquid $(CH_3CH.OEt)_2O$ (153° cor.) S.G. ^{11} ·891. This is sparingly sol. water. It decomposes in a few days into acetal and aldehyde: $(CH_3CH.OEt)_2O = CH_3.CH(OEt)_2 + CH_3.CHO$.—5. Dry NaOEt gives $CH_3.CH(OEt).O.CHCl.CH_3$ (146°), a liquid, decomposed by hot water (Hanriot, *A. Ch.* [5] 25, 223).—6. MeOH and NaOMe form similarly $(CH_3CH.OMe)_2O$ (126°–127°). S.G. $^{12\cdot5}$ ·953. This also has an aromatic smell and splits up like the foregoing, though more slowly, into dimethyl acetal and aldehyde.—7. *Sodium succinate* gives $O(CHMe.OCO)_2C_2H_4$ (Geuther, *A.* 226, 228).—8. *Zinc ethyl* produces di-butyl oxide $(CH_3.CHEt)_2O$.

Tri-chloro-di-ethyl oxide $CHCl_2.CHCl.OEt$. (157°) (G.); (168°) (K.). From chloro-vinyl ethyl oxide and Cl (Godefroy, *C. R.* 102, 869). Also from di-chloro-acetal and PCl_5 (Krey, *J.* 1876, 475). Occurs in the product of chlorination of ether. Fuming liquid; with NaOEt it gives $CHCl_2.CH(OEt)_2$. Conc. aqueous KOH gives $CCl_2:CH.OEt$ (145°).

Tetra-chloro-di-ethyl oxide $CCl_3.CHCl.OEt$. Mol. w. 212. (190°) (P. a. P.); (c. 183°) (G.). S.G. ^{0} 1·437; ^{15} 1·418.

Formation.—1. From chlorine and ether at 90° in the dark.—2. From chloral alcoholate and PCl_5 (Henry, *B.* 4, 101, 435; Paternò a. Pisati, *J.* 1872, 303; *G.* 2, 333).—3. From dichloro vinyl ethyl oxide $CCl_2:CH.OEt$ and chlorine (Godefroy, *C. R.* 102, 869).

Reactions.—1. Con. H_2SO_4 gives chloral, HCl, and alcohol.—2. Heated with *alcohol* it gives tri-chloro-acetal $CCl_3CH(OEt)_2$.—3. With dilute (10 p.c.) *alcoholic potash* it gives trichloro-vinyl-ethyl oxide $CCl_2:CCl.O.Et$.—4. H_2S gives $C_4H_6S_2O$ [123°] and $C_4H_6Cl_2SO$ [72°] (Malaguti, *A.* 32, 29).

Penta-chloro-di-ethyl oxide $CCl_3.CCl_2.OEt$. (190°–210°). S.G. 1·65.

Formation.—1. The final product of the action of chlorine on ether in the dark (Jacobsen, *B.* 4, 217).—2. From $CCl_2:CCl.OEt$ and Cl (Busch, *B.* 11, 445). It is partly decomposed on boiling.

Penta-chloro-di-ethyl oxide
$CCl_3.CHCl.O.CH_2.CH_2Cl$. (235°). S.G. ^{8}: 1·577. From PCl_5 and $CCl_3.CH(OH).O.CH_2.CH_2Cl$, a compound of chloral and glycolic chlorhydrin (Henry, *B.* 7, 763).

Hexa-chloro-di-ethyl oxide $(CHCl_2.CHCl)_2O$. (250). From PCl_5 and the hydrochloride of di-chloro-aldehyde (Paternò a. Pisati, *G.* 1, 461).

Octo-chloro-di-ethyl oxide $C_4H_2Cl_8O$. Formed by the action of Cl on aldehyde hydrochloride in sunlight.

Crystals, smelling like camphor, may be sublimed (Roth, *B.* 8, 1017).

Per-chloro-di-ethyl oxide $C_4Cl_{10}O$. [69°]. S.G. ^{15} 1·900. Formed by the action of chlorine in sunlight on ether (Regnault, *A.* 34, 27; Malaguti, *A. Ch.* [3] 16, 4). Dimetric octahedra (Nicklès, *A. Ch.* [3] 22, 28). Splits up on heating into C_2Cl_6 and trichloro-acetyl chloride.

CHLORO-ETHYL-OXY-TOLUQUINOLINE *v.* CHLORO-OXY-METHYL-ETHYL-QUINOLINE.

ω-**CHLORO-DI-ETHYL-DI-PHENYL-ETHANE** $C_{18}H_{21}Cl$ *i.e.* $CH_2Cl.CH(C_6H_4Et)_2$. (c. 268°). From ethyl-benzene, $CH_2Cl.CHCl.OEt$, and H_2SO_4 (Hepp, *B.* 7, 1414). On distillation it gives HCl and $C_{18}H_{20}$.

Eso-**CHLORO-ETHYL-PHENYL METHYL KETONE** $C_6H_3EtCl.CO.CH_3$. Formed, together with the two chloro-phthalic acids, by oxidising chloro-di-ethyl-benzene with chromic mixture (Istrati, *A. Ch.* [6] 6, 421). Liquid; not attacked by boiling alcoholic KOH, but converted into chloro-ethyl-benzoic acid by potash-fusion.

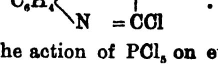
CHLORO-TETRA-ETHYL-PHOSPHONIUM CHLORIDE $(ClCH_2.CH_2)PEt_3Cl$. From PEt_3 and ethylene chloride in the cold (Hofmann, *A. Suppl.* 1, 276). Needles. Moist Ag_2O converts it into an oxy-ethyl base $CH_2(OH).CH_2.PEt_3OH$.

Salt.—$(C_2H_4Cl.PEt_3Cl)_2PtCl_4$. Orange needles.

CHLORO-ETHYL-PROPYL-GLYOXALINE $C_8H_{13}ClN_2$. *Chlor-oxal-propyline* (236° cor.). V.D. = 5·65 (obs.). S.G. ^{16} 1·09. From di-propyl oxamide by PCl_5. Oil. V. sl. sol. water, miscible with alcohol, ether, or $CHCl_3$. On reduction with HI it gives ethyl-propyl-glyoxaline (Wallach a. Schulze, *B.* 13, 516; 14, 423; *A.* 214, 312).

Salts.—$(B'HCl)_2PtCl_4$.—$B'HI$.—B'_2AgNO_3: needles.

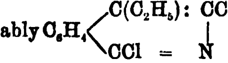
(*Py.* 3, 2)-**CHLORO-ETHYL-QUINOLINE**



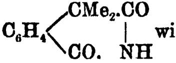
$$C_{11}H_{10}ClN \text{ i.e. } C_6H_4\left\langle\begin{array}{l}CH=C(C_2H_5)\\ \quad\quad\;\;|\\ N\;\;=CCl\end{array}\right. \quad [78°].$$

Prepared by the action of PCl_5 on ethyl-hydrocarbostyril (Baeyer a. Jackson, *B.* 18, 120). Insol. water, v. sol. other solvents. Volatile with steam. Weak base.—$(B'HCl)_2PtCl_4$. V. sol. alcohol, decomposed by water.

Chloro - ethyl(?) - isoquinoline $C_{11}H_{10}NCl$. [c. 80°]. Formed by boiling the di-chloro-derivative [166°] with HI and P. Colourless crystals. By heating with HI and P to 200° it is completely dechlorinated (Gabriel, *B.* 20, 1206).



Di-chloro-ethyl(?)-isoquinoline $C_{11}H_9NCl_2$ probably $C_6H_4\left\langle\begin{matrix}C(C_2H_5):CCl\\ | \\ CCl = N\end{matrix}\right.$ [166°]. Formed by heating the imide of phenyl-di-methyl-carboxylic acid $C_6H_4\left\langle\begin{matrix}CMe_2.CO\\ | \\ CO.\ NH\end{matrix}\right.$ with $POCl_3$; if the product is a derivative of ethyl-isoquinoline an isomeric change must have occurred during the reaction. Long colourless needles. By HI and P it is first reduced to the mono-chloro-derivative [80°] and then to the ethyl(?)-isoquinoline [65°] (Gabriel, *B.* 20, 1206).



DI-CHLORO-DI-ETHYL SULPHIDE $(CH_2Cl.CH_2)_2S$. (217°). Formed by the action of PCl_5 on $S(CH_2.CH_2OH)_2$ obtained from glycol chlorhydrin and K_2S (V. Meyer, *B.* 19, 3259; 20, 1729). Oil. Very poisonous and violently inflames the skin (difference from di-ethyl sulphide).

Tetra-chloro-di-ethyl sulphide $(C_2H_3Cl_2)_2S$. (167°–172°). S.G. $\frac{12}{}$ 1·547. A yellow oil formed by passing chlorine into di-ethyl sulphide, which is at first kept cool and in the shade (Riche, *A.* 92, 358). There appear also to be formed $(C_2H_2Cl_3)_2S$ (189°–192°), $(C_2HCl_4)_2S$ (217°–222°) and $(C_2Cl_5)_2S$ (?).

Di-chloro-di-ethyl di-sulphide $(CH_2Cl.CH_2)_2S_2$. S.G. $\frac{19}{}$ 1·346. From ethylene and Cl_2S_2 at 100° (Guthrie, *A.* 119, 91; 121, 108). Pale yellow oil. Alcoholic KOH gives oily $(CH_2OH.CH_2)_2S$. HNO_3 forms $CH_2Cl.CH_2.SO_3H$ (Spring a. Lecrenier, *Bl.* [2] 48, 629).

Tetra-chloro-di-ethyl di-sulphide $(C_2H_3Cl_2)_2S_2$. S.G. $\frac{11}{}$ 1·599. Formed by passing ethylene through boiling S_2Cl_2 (G.). Oil.

CHLORO-ETHYL SULPHOCYANIDE $Cl.C_2H_4.CNS$. (203°). Formed by heating $C_2H_4Br_2$ (100 g.), KCNS (66 g.) and alcohol (250 c.c.) with inverted condenser. The product is filtered, distilled to 150° and the residue in the retort cooled in a freezing mixture. $C_2H_4(CNS)_2$ now crystallises out. The liquid portion is distilled (J. W. James, *C. J.* 35, 807, *J. pr.* [2] 20, 352; 31, 411). Formed in the same way from ethylene chloro-bromide (107°–109°) (James, *C. J.* 43, 39; 47, 365).

Properties.—Oil. Smells like mustard oil. Burns with violet flame. Soluble in alcohol and ether. Dissolves in hot water, but separates again on cooling.

Reactions.—1. Fuming HNO_3 converts it into chloro-ethane sulphonic acid, $Cl.C_2H_4.SO_3H$. Ammonia, of course, will convert this into taurine.—2. Alcoholic *potassic sulphocyanide* converts it into $C_2H_4(SCN)_2$.—3. With aqueous Na_2SO_3 in sunlight it forms $C_2H_4(SCN)(SO_3Na)$.

DI-CHLORO-(a)-ETHYL-THIOPHENE $C_4H(C_2H_5)Cl_2S$ (236° cor.). A liquid formed by passing chlorine into cooled 'β'-ethyl-thiophene (Bonz, *B.* 18, 551).

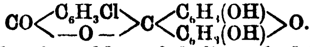
DI-CHLORO-ETHYL-TOLUENE (?). $C_9H_{10}Cl_2$. (365°). Formed, together with propylene and chlorinated cresol by distillation of penta-chloro-thymol (Lallemand, *C. R.* 43, 375).

DI-CHLORO-EUXANTHIC ACID v. EUXANTHIC ACID.

DI-CHLORO-FLUORENE $C_{13}H_8Cl_2$. [128°]. Formed by passing chlorine into fluorene (from coal-tar) in chloroform (Hodgkinson a. Matthews, *C. J.* 43, 170). Colourless plates. Oxidised by chromic mixture to di-chloro-di-phenylene ketone [158°].

Tri-chloro-fluorene $C_{13}H_7Cl_3$ [147°]. Formed by leading chlorine into a CS_2 solution of fluorene for a long time (Holm, *B.* 16, 1082). White plates. Sl. sol. alcohol and ether.

Penta-chloro-fluorene di-chloride $C_{13}H_5Cl_7$ [104°]. From di-chloro-fluorene in chloroform by chlorine (H. a. M.). Long needles. CrO_3 converts it into a yellow ketone (?) [104°]. Alcoholic KOH converts it into a red body (? $C_{13}H_5Cl_5$) which is insol. alcohol, but crystallises from chloroform, petroleum or acetic acid [c. 110°]. It is not attacked by HNO_3 or CrO_3.



CHLORO-FLUORESCEÏN $CO\left\langle\begin{matrix}C_6H_3Cl\\ —O—\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}\right\rangle O$. Formed by heating chloro-phthalic anhydride [97°] with resorcin. V. sl. sol. water and $CHCl_3$. When freshly prepared it is sol. alcohol and ether, but it changes on keeping into an insoluble crystalline form; v. sol. acetic acid; insol. C_6H_6; sol. aqueous KHO, and K_2CO_3 forming a deep red solution, which when diluted shows a fluorescence like that of fluoresceïn (Graebe a. Rée, *C. J.* 49, 530).

Di-chloro-fluoresceïn. *Hydrate.* $C_6H_2Cl_2:C_2O_2:(C_6H_3(OH)_2)_2$. Formed by heating ($\beta$)-di-chloro-phthalic anhydride [151°] with resorcin at 200°. Loses aq when heated. Alkalis form a red solution with green fluorescence (Le Royer, *A.* 238, 357).

Tetra-chloro-fluoresceïn $C_6Cl_4:C_2O_2:(C_6H_4OH)_2O$. Formed by heating resorcin with tetra-chloro-phthalic anhydride (Graebe, *A.* 238, 333). Addition of acids to its solution in NaOH pps. the hydrate or ortho-compound, which at 180° is dehydrated. Insol. ether.

Diacetyl derivative $C_6Cl_4:C_2O_2:(C_6H_4OAc)_2O$.

Hydrate $C_6Cl_4:C_2O_2:(C_6H_4(OH)_2)_2$. Ppd. by adding acids to a solution of the fluoresceïn in aqueous NaOH. Orange needles (from ether); insol. water, sl. sol. alcohol. Its alkaline solution is red with strong green fluorescence like fluoresceïn. At 180° it gives off H_2O.

Chloride $C_6Cl_4:C_2O_2:(C_6H_3Cl)_2O$. [259°].

CHLOROFORM $CHCl_3$. *Tri-chloro-methane.* Mol. w. 119½. [–70°] (Berthelot, *Bl.* [2] 29, 3). (60·9°) at 754·3 mm. (Schiff, *A.* 220, 95); (61·4°) (Thorpe); (62°) (Perkin, *C. J.* 45, 530). S.G. $\frac{11·8}{4}$ 1·5039; $\frac{60·9}{4}$ 1·4081; $\frac{15}{15}$ 1·5009; $\frac{35}{35}$ 1·4849. C.E. (11·8 to 60·9) ·00138 (Schiff); (0°–10°) ·001248 (Thorpe); (0°–50°) ·0013368 (T.); see also Grimaldi, *G.* 17, 18. S. ·987 at 0°; ·775 at 55° (Chancel a. Parmentier, *C. R.* 106, 577). V.D. 4·12 (for 4·12). H.F.p. 24110 (*Th.*). H.F.v. 23530. M.M. 5·559 at 15·3°. S.H. ·233 (Schüller, *P. Suppl.* 5, 116, 192). μ_D 1·451 (Forbes, *P. M.* [3] 35, 94). S.V. 84·6 (Schiff); 85·6 (Ramsay); 84·5 (Thorpe). *Capillarity*: Swan, *C. J.* 1, 174; *P. M.* [3] 33, 36. *Compressibility*: Grassi, *A. Ch.* [3] 31, 437.

Formation.—1. By the action of bleaching-powder on dilute alcohol (Soubeiran, *A. Ch.* [2] 48, 131; Soubeiran a. Mialhé, *A.* 71, 225) or on acetone (Liebig, *A.* 1, 198).—2. By the action of chlorine on marsh-gas in daylight, and ultimately in sunlight (Regnault, *A. Ch.* [2] 71, 380).—3. By passing a mixture of chlorine and methyl chloride through animal charcoal at 250°-350° (Damoiseau, *C. R.* 92, 42). 4. By the action of aqueous potash on chloral (Liebig, *A.* 1, 199).—5. By the action of nascent hydrogen on CCl_4.—6. By boiling tri-chloro-acetic acid with aqueous alkalis (Dumas, *A. Ch.* [2] 56, 115; *A.* 32, 113).—7. From iodoform and PCl_5 (Gautier, *Bl.* [2] 13, 316).—8. From CCl_4, zinc, and dilute H_2SO_4 (Geuther, *A.* 107, 212).

Preparation.—1. By mixing chloral with dilute caustic soda.—2. Bleaching powder (40 pts.), water (100 to 150 pts.), alcohol (4 to 10 pts.), and slaked lime (4 to 10 pts.) are distilled together. The distillate separates into two layers, the lower one being chloroform. This is freed from chlorine by shaking with potash, dried over $CaCl_2$ and rectified (Kessler, *J. Ph.* [3] 13, 162).

Theory of the process.—The bleaching powder is supposed first to convert the alcohol into chloral (*q. v.*), and the lime which is present (or formed) would then split this up into calcic formate and chloroform: $8CaO.Cl_2 + 2C_2H_6O = 2C_2Cl_3HO + 5CaCl_2 + 3CaO + 5H_2O = 2CCl_3H + Ca(CHO_2)_2 + 5CaCl_2 + 2CaO + 4H_2O$.

When alcohol of various strengths is poured on bleaching powder the distillate, which sometimes explodes after shaking well with water, gives an oil which can be separated by fractionating into the following portions:—

Fraction	1 pt. alcohol mixed with pts. of water					
	0	1	2	4	8	
60°-70°	2·4	3·4	56·5	89·1	98·1	percentage composition of oil.
70°-80°	9·8	12·4	31·2	7·8	1·9	
80°-100°	12·3	31·6	12·2	3·1	—	
100°-150°	21·0	27·5	—	—	—	
150°-160°	50·6	24·9	—	—	—	
160°-180°	4·2	—	—	—	—	

The amount of chloro-acetal (150°-160°) is therefore greatly diminished by diluting the alcohol (Goldberg, *J. pr.* 132, 111). The yield of chloroform is never more than equal in weight to the weight of the alcohol used, this is less than one molecule of chloroform from two molecules of alcohol. Chloroform cannot be prepared from pure methyl alcohol by means of bleaching powder, although it is formed from commercial methyl alcohol (Belohoubek, *A.* 165, 349). Chlorinated compounds are formed by the action of bleaching powder on isopropyl, isobutyl, and isoamyl alcohols; so that the alcohol used to prepare chloroform should not contain fousel oil (J. Regnault a. E. Hardy, *J. Ph.* [4] 30, 405).

Properties.—Characteristic odour and sweet taste, almost insoluble in water. When pure it is not turned brown by H_2SO_4. Chloroform reduces Fehling's solution, thus: $CHCl_3 + 2CuO + 5KHO = Cu_2O + 3KCl + K_2CO_3 + 3H_2O$ (Baudrimont, *J. Ph.* [4] 9, 410). It dissolves fats and resins. A solution of iodine in chloroform is violet, but bromine forms a red solution. It is anæsthetic (James Simpson, *A.* 65, 121) and antiseptic (Robin, *C. R.* 30, 52; Augendre, *C. R.* 3., 679). When a mixture of chloroform and water is kept at 0° for a long time with frequent shaking a hydrate $CHCl_3$,18aq separates in long laminæ. It is lighter than chloroform but heavier than water, and melts at 1·6° (Chancel a. Parmentier, *C. R.* 100, 27; *cf.* Sajohelyi a. Ballo, *B.* 4, 160).

Detection.—Chloroform may be distinguished from most other similar chlorinated hydrocarbons by boiling it with alcoholic potash and a primary amine (*e.g.* aniline), when the characteristic disgusting odour of the carbamines will be noticed (Hofmann, *B.* 3, 769). When the vapour of chloroform is passed through a red-hot tube chlorine is liberated, and will turn paper moistened with starch and potassium iodide blue (Ragsky, *J. pr.* 46, 170; Luedeking, *Am.* 8, 358). Chloroform gives a reddish-purple colour (? rosolic acid) when poured upon the hot residue obtained by evaporating an alcoholic solution of phenol mixed with caustic potash (Guareschi, *G.* 3, 401).

Impurities.—Chloroform that is to be used for surgical operations should not give any brown colour when shaken with H_2SO_4 (Gregory, *Pr. E.* 1850, 391; *cf.* Vulpius, *Ar. Ph.* [3] 13, 37; 25, 998). The presence of alcohol causes opalescence when chloroform is mixed with water (Mialhé, *J. Chim. Méd.* [3] 4, 279), and a green colour with chromic mixture (Cottell, *J. Ph.* [3] 13, 359). The reduction of potassium permanganate may also be used as a rough index of the amount of alcohol, aldehyde, and other oxidisable substances present in chloroform (Jolles, *Chem. Zeit.* 11, 786).

Estimation.—By treating a chloroform solution with alcoholic potash the chlorine is obtained as chloride. The conditions for getting a theoretical yield have been determined by De Saint-Martin (*C. R.* 106, 492-496; *cf.* Chancel a. Parmentier, *C. R.* 106, 577).

Reactions.—1. CrO_3 mixture gives $COCl_2$.—2. *Zinc* and dilute H_2SO_4 convert it into CH_2Cl_2 (Geuther, *A.* 107, 212; Richardson a. Williams, *C. N.* 18, 60).—3. *Zinc-dust* converts it in presence of ammonia into methane (Perkin, *C. N.* 18, 106).—4. Boiled with *alcoholic potash* it forms potassium chloride and formate, thus: $CHCl_3 + 4KHO = 3KCl + CHO_2K + 2H_2O$.—5. With *sodic ethylate* it gives orthoformic ether, $CH(OEt)_3$ (Williamson a. Kay, *C. J.* 7, 224).—6. Mixed with ammonia and passed through a red-hot tube it reacts thus: $CHCl_3 + NH_3 = CNH + 3HCl$. Aqueous *ammonia* at 220° forms carbonic oxide, ammonium formate, and ammonic chloride, thus: $2CHCl_3 + 7NH_3 + 3H_2O = CO + 6NH_4Cl + HCO_2NH_4$ (André, *C. R.* 102, 553).—7. *Water* at 220° forms CO, formic acid, and HCl.—8. Alcoholic K_2S forms potassium thioformate H.CO.SK (Nicol, *Tr. E.* 29, 531).—9. *Aniline* at 190° gives di-phenyl-form-amidine $C_6H_5NH.CH{:}N.C_6H_5$ (Hofmann, *Pr.* 9, 229).—10. *Bromine* at 200° gives $CBrCl_3$ (Paternò, *G.* 1, 593; Friedel a. Silva, *Bl.* [2] 17, 537).—11. With *bromine* (3 pts.) and *iodine* (1 pt.) at 150° it gives CBr_3Cl [70°] and CBr_4 [76°] (Bolas a. Groves, *C. J.* 24, 779). 12. HNO_3 containing NO_2 forms at 100° a small quantity of chloropicrin (Mills, *C. J.* 24, 641).—13. Conc. HIAq at 125° gives CH_2I_2 (Lieben, *Z.* [2] 4, 713). PH_4I and ZnO give CH_3Cl (Hofmann, *B.* 6, 301).—14. When passed over *red-hot copper* some acetylene is formed (Berthelot, *C. R.* 50, 805). –15. *Potassium amalgam* also forms acetylene (Kletzinsky, *Z.* [2] 2, 127).—16. K_2SO_3 at 170° forms $CH_2(SO_3K)_2$ and $CH(SO_3K)_3$ (Strecker, *Z.* [2] 4, 214).—17. *Sodium* acting on chloroform containing alcohol forms chlor-ethulmic acid $C_6H_9ClO_2$ (Hardy, *A. Ch.* [3] 65, 340; *C. R.* 54, 470; *cf.* Kern, *C. N.* 31, 121).—18. The *copper-zinc couple* does not act on pure chloroform; in presence of alcohol at 60° methane is evolved, together with a small quantity of acetylene; in presence of water methane is evolved even at 12° (Gladstone a. Tribe, *C. J.* 28, 508).—19. $SbCl_5$ at 100° forms CCl_4 (Lossner, *J. pr.* [2] 13, 418).—20. Electric sparks decompose chloroform forming HCl and C_2Cl_6; in presence of air $COCl_2$ is formed (J. Regnault, *J. Ph.* [5] 5, 504).—21. Potash added to a mixture of *acetone* (1 mol.) and chloroform (1 mol.) forms acetone-chloroform or oxy-isobutyro-tri-chloride $(CH_3)_2C(OH).CCl_3$. There is also formed a liquid isomeride, possibly $CHCl_2.CMe_2.OCl$, (170°). It is a strong poison and yields with benzene and Al_2Cl_6 chloro-di-phenyl-*tert*-butyl alcohol (239°); while with PCl_5 it yields $C_4H_6Cl_2O$ (151°) (Willgerodt a. Genieser, *J. pr.* [2] 37, 362). Potash (8 mols.) acting on chloroform (1 mol.) and acetone (2 mols.) forms $C_{11}H_{20}O_6$ *i.e.* $CMe_2(O.CMe_2.CO_2H)_2$; an acid which, like acetone-chloroform (*q. v.*), is converted into oxy-isobutyric acid by heating with water (Willgerodt, *B.* 20, 2445; *Bl.* [2] 39, 157; Engel, *Bl.* [2] 47, 499; *C. R.* 104, 688).—22. With SO_3 it forms carbonic oxide, $ClSO_3H$ and $Cl_2S_2O_5$ (Armstrong, *Z.* 1870, 247).

Combination.—With aqueous H_2S at 0° it forms a crystalline compound $CHCl_3,2H_2S$ 23aq (Loir, *C. R.* 34, 547; *J.* 1852, 560; Forcrand, *A. Ch.* [5] 28, 12).

CHLORO-FORMIC ACID *Cl.CO.OH.

Methyl ether. $Cl.CO_2.Me$. (71° cor.). S.G. ^{15} 1·236 (Roese, *A.* 205, 228). Formed by the action of $COCl_2$ on methyl alcohol (Dumas, *A.* 10, 277; *A. Ch.* 58, 52; Meyer a. Wurster, *B.* 6, 965). Formed also by the action of chlorine on gaseous methyl formate (Hentschel, *J. pr.* [2] 36, 211). *Preparation.*—To avoid formation of methyl carbonate proceed thus: Phosgene is freed from chlorine by passing through a flask full of pieces of antimony and powdered glass and placed in the water bath. The gas is passed into a few c.c. of chloro formate of methyl at 0°. Methyl alcohol is added in small portions at a time, waiting each time until the phosgene goes through unabsorbed. Altogether not more than 150 c.c. of methyl alcohol should be used (A. Klepl, *J. pr.* [2] 26, 447). *Properties.*—Heavy oil; readily decomposed by boiling with water. Gives the tri-chloro-methyl ether when chlorine acts on it in sunlight. Intermediate compounds are $C_4H_3Cl_5O_4$ and $C_8H_9Cl_7O_8$. The compound $C_4H_3Cl_5O_4$ (109° cor.) is a very pungent oil, S.G. $\frac{27}{27}$ 1·4741; $\frac{14}{14}$ 1·4786. It is decomposed by water into formic aldehyde, $2CO_2$, and CO; while aniline forms $C_4H_4Cl_3(NPhH)_2O_4$ [45°]; and fusion with NaOAc yields methylene diacetate (166°). The other compound, $C_8H_9Cl_7O_8$ or $C_6H_7Cl_5O_6$, (181° cor.), S.G. 1·52, is a liquid, slowly decomposed by boiling water into CO, CO_2, HCl, and formic aldehyde (Hentschel, *J. pr.* [2] 36, 468).

Tri-chloro-methyl ether CCl_3A'. (128° cor.). S.G. ^{14} 1·653. V D. 94·3 (calc. 99). Formed by chlorinating methyl formate in sunlight. Liquid; inflames the skin. Above 300° it changes into the isomeric $COCl_2$; this change takes place slowly even on boiling. At a dull red heat it splits up into CCl_4 and CO_2. Al_2Cl_6 decomposes it in the same way (Hentschel, *J. pr.* [2] 36, 99, 305). *Reactions.*—1. Like $COCl_2$, it acts on NaOAc forming NaCl, CO_2, and Ac_2O.—2. MeOH forms an oil, possibly $CCl_3O.CO.OMe$; it boils at 164° being split up into $COCl_2$ and $Cl.CO_2Me$.—3. Dry and aqueous *ammonia* forms urea but not tri-chloro-acetamide.—4. *Aniline* forms di-phenyl-urea and phenyl cyanate.—5. *Benzene* and Al_2Cl_6 give $(C_6H_5)_3CCl$.—6. *Phenol* gives $C_6H_5O.CO.Cl$.

Ethyl ether $Cl.CO_2Et$. Mol. w. 108½. (94°). S.G. ^{15} 1·139. V.D. 3·82. *Preparation.*—By passing $COCl_2$ into well-cooled alcohol (Dumas, *A. Ch.* [2] 54, 226; Cloez, *A. Ch.* [3] 17, 303; Cahours, *A. Ch.* [3] 19, 316; Klepl, *J. pr.* [2] 26, 448; Wilm a. Wischin, *A.* 147, 150); or by dropping alcohol into liquid $COCl_2$ standing in a freezing-mixture (Hentschel, *B.* 18, 1177). *Properties.*—Pungent liquid; decomposed by hot, but not by cold, water. *Reactions.*—1. With *alcohol* it forms carbonic ether, reacting thus: $ClCO_2Et + HOEt = EtO.CO_2Et + HCl$. — 2. With *sodium* it reacts in this way: $2ClCO_2Et + Na_2 = 2NaCl + CO + CO_3Et_2$.—3. With $ZnMe_2$ it reacts in the following manner: $2ClCO_2Et + ZnMe_2 = ZnCl_2 + 2CO_2 + 2C_2H_4 + 2CH_4$ (Butlerow, *Z.* 1863, 484).—4. With *ammonia* it forms carbamic ether, $NH_2.CO_2Et$.—5. Al_2Cl_6 splits it up into CO_2 and EtCl.—6. *Benzene* and Al_2Cl_6 give ethyl-benzene (Rennie, *C. J.* 41, 33).—7. $ZnCl_2$ gives CO_2, EtCl, HCl, and ethylene (Ulsch, *A.* 226, 281).—8. *Sodium amalgam* converts it into formic acid (Geuther, *A.* 205, 225).—9. $NaOC_6H_5$ gives $(C_6H_5O)CO(OEt)$ (Fatianoff, *Z.* 1864, 77).—10. Na_2S gives $S(CO_2Et)_2$ (V. Meyer, *B.* 2, 297).—11. *Potassium cyanate* forms the following crystalline bodies: (*a*) $C_{12}H_{15}N_3O_9$ or $C_3N_3O_3(CO_2Et)_3$ [119°]; (*b*) $C_{11}H_{15}N_3O_7$ or $C_3N_3O_3Et(CO_2Et)_2$ [123°]; (*c*) $C_{10}H_{15}N_3O_5$ or $C_3N_3O_3Et_2(CO_2Et)$ [107°]; (*d*) $NH(CO_2Et)_2$ [50°]; and (*e*) $C_3N_3O_3Et_3$ (Wurtz a. Henninger, *C. R.* 100, 1419; *Bl.* [2] 44, 26).—12. With KNCS in presence of alcohol it forms carbonic ether and allophanic ether (Wilm, *A.* 192, 243): $2Cl.CO_2Et + 2KNCO + 3HOEt = 2KCl + 2Et_2CO_3 + C_2H_3N_2O_3Et$.—13. With *thio-urea* it forms $NH_2.CS.NHCO_2Et,HCl$ [117°] (Pawlewski, *B.* 21, 401).—14. With *di-phenyl-thio-urea* it forms di-phenyl-thio-allophanic acid $NHPh.CS.NPh.CO_2Et$.—15. With *phenyl-thio-urea* it forms phenyl-allophanic acid $NHPh.CS.NH$ CO_2Et.—16. With *acetyl-phenyl-thio-urea* it forms α-phenyl-thio-allophanic acid $NH_2CS.NPh.CO_2Et$.—17. *Cyanethine* forms cyanethine carboxylic acid (E. v. Meyer a. Schöne, *J. pr.* [2] 30, 123).—18. *Quinoline* forms ethyl-quinoline: $C_9H_7N + ClCO_2Et = C_9H_6EtNHCl + CO_2$ (M. a. S.).

Chloro-ethylic ether $Cl.CO_2.CH_2.CH_2Cl$. (150°–160°). From glycolic chlorhydrin and $COCl_2$ in the cold (J. Nemirowsky, *J. pr.* [2] 31, 173). The product is mixed with K_2CO_3 and extracted with ether. Colourless, fuming, pungent liquid, insol. water, sol. alcohol and ether. *Reactions.*—1. Not decomposed by boiling *water*. 2. Converted by boiling dilute *potash* into glycol, potassium chloride, and potassium carbonate.—3. Converted by *ammonia* into the carbamate of chloro-ethyl, as follows: $Cl\ CO.O.C_2H_4Cl + 2NH_3 = NH_4HCl + H_2N.CO.O.C_2H_4Cl$.—4. With *aniline* it reacts, forming the corresponding compound $NPhH.CO_2C_2H_4Cl$ (phenyl-carbamic acid).

Propyl ether $ClCO_2Pr$. (115° cor.). S.G. ^{15} 1·09. Liquid; more stable than methyl ether (Roese, *A.* 205, 229).

Isopropyl ether $ClCO_2Pr$. (95°). S.G. ^{4} 1·144 (Spica, *G.* 17, 168). Gives with NH_3 isopropyl carbamate $NH_2.CO_2Pr$ [37°].

Isobutyl ether $ClCO_2C_4H_9$. (129° cor.). S.G. ^{15} 1·053 (Roese; *cf.* Mylius, *B.* 5, 972). Ammonia converts it into isobutyl carbamate $NH_2.CO_2C_4H_9$ [55°].

Amyl ether $Cl.CO_2C_5H_{11}$. (153°) (S.); (154° cor) (R.). S.G. ^{15} 1·032. From $COCl_2$ and amyl alcohol (Schöne, *J. pr.* [2] 32, 246).

Phenyl ether $Cl.CO_2C_6H_5$. (187°). From the tri-chloro-methyl ether and NaOPh (Hentschel, *J. pr.* [2] 36, 316).

Amide $Cl.CO.NH_2$. [50°]. (62°). Formed by passing dry $COCl_2$ into NH_4Cl at 400° (Gattermann a. Schmidt, *B.* 20, 858). Flat needles, with unpleasant odour. Changes on keeping into cyamelide with evolution of HCl. Decomposed by water into CO_2 and NH_4Cl. With toluene and Al_2Cl_6 it gives the amide of *p*-toluic acid; other aromatic hydrocarbons and phenol ethers act similarly. Amines yield alkyl-ureas. Aqueous NaOH forms cyanic acid. Alcohols in small quantities form allophanic ethers, in excess they give carbamic ethers.

Methylamide Cl.CO.NHMe '*Methyl-urea-chloride.*' [90°]; (94°); colourless plates. Obtained by passing carbonyl chloride $COCl_2$ over dry methylamine hydrochloride heated to 140°. Distilled over lime it yields methyl cyanate OC:NMe. Decomposed by water.

Ethylamide Cl.CO.NHEt '*Ethyl-urea-chloride.*' (92°); colourless liquid. Obtained by passing $COCl_2$ over dry ethylamine hydrochloride heated to 250°–270°. Distilled over lime it yields ethyl cyanate OC:NEt. On conversion into vapour it dissociates into ethyl cyanate and HCl, which recombine on cooling. In most of its reactions it gives the same products as ethyl cyanate (Gattermann a. Schmidt, *B.* **20**, 118; *A.* 244, 34).

Di-methyl-amide $Cl.CO.NMe_2$. Colourless liquid. Sol. C_6H_6, ether, and CS_2. Prepared by the action of carbonyl chloride ($COCl_2$) on dimethylamine. Is slowly decomposed by water into CO_2 and $NHMe_2HCl$ (Michler a. Escherich, *B.* 12, 1162).

CHLORO-FORMYL-TRICARBOXYLIC ACID *v.* CHLORO-METHANE-TRICARBOXYLIC ACID.

CHLORO-FUMARIC ACID $C_2HCl(CO_2H)_2$. [191°].

Preparation.—1. Chlorine is passed to saturation into succinyl chloride. Methyl alcohol is added to the product as long as HCl escapes. The liquid is then boiled. On cooling, methyl chloro-fumarate, [102°], separates. The filtrate is poured into water, when a further quantity of this body is thrown down. HCl at 140° decomposes the ether forming the acid (Kauder, *J. pr.* [2] 31, 24).—2. Tartaric acid (50 g.) and PCl_5 (275 g.) are heated with inverted condenser. The product is distilled to 180° and the residue mixed with water. The solution is shaken with ether and the ether evaporated (Perkin a. Duppa, *A.* 115, 105; 129, 373; *C. J. Proc.* 4, 75).

Properties.—Clumps, from alcohol and benzene. V. sol. water, alcohol, and ether, sl. sol. benzene and ligroïn. May be sublimed unaltered.

Constitution.—Perkin considers it to be a derivative of fumaric acid because it is very soluble in water. The fact that it sublimes without forming an anhydride would indicate that it is a derivative of maleic acid (Kauder).

Reactions.—1. *Sodium amalgam* forms succinic acid (Perkin, *A.* 129, 375).—2. Dissolved in cold water and the equivalent of *aniline* added it gives a crystalline pp. of the acid aniline salt, $CO_2H.CH.CCl.CO_2H.NH_2.Ph$. [178°]. An aqueous solution may be kept for weeks without undergoing any change. On boiling the aqueous solution, it behaves like the corresponding bromo-fumarate, although less readily (Michael, *Am.* 9, 180).

Salts.—KHA″. Transparent prisms.—BaA″ 3aq. Clumps.—Ag_2A''.

Methyl ether. Me_2A''. (224°).

Ethyl ether. Et_2A''. (245°). S.G. ^{20} 1·178. From tartaric ether and PCl_5 (Henry, *A.* 156, 178; Claus, *A.* **191**, 80).

Amic ether $C_2HCl(CO_2Et)(CONH_2)$. [102°]. From chlorofumaric ether and alcoholic NH_3 (Claus a. Voeller, *B.* 14, 150). Tables.

Imide C_4HClO_2NH. [131°]. Large colourless plates. Sol. water, alcohol and ether. Formed by chlorination of succinimide (Ciamician a. Silber, *B.* 16, 2394).

Chloro-fumaric acid $C_2HCl(CO_2H)_2$ [178°]. (c. 190°). White pp. consisting of microscopic needles. V. sol. alcohol, water, and ether. Formed by the combination of acetylene-di-carboxylic acid with HCl.

Salts.—$A''K_2$: large sparingly soluble prisms.—$A''Ag_2$ aq: fine crystalline pp.—A″Pb 2aq: amorphous pp. becoming crystalline (Baudrowski, *B.* **15**, 2695).

V. also CHLORO-MALEIC ACID.

TETRACHLOROGALLEÏN $C_{20}H_{10}Cl_4O_9$. From tetra-chloro-phthalic anhydride and pyrogallol at 200° (Graebe, *A.* 238, 337). At 180° it gives off 2aq becoming $C_{20}H_6Cl_4O_7$.

CHLOROGENINE *v.* ALSTONINE.

β-CHLORO-GLUTACONIC ACID $HO_2C.CH{:}CCl.CH_2.CO_2H$. [129°]. Formed by the action of PCl_5 (16 pts.) upon acetone-di-carboxylic ether $CO(CH_2CO_2Et)_2$ (5 pts.) at 100°, and saponification of the ether with conc. HCl; yield: 50–60 p.c. of the theoretical. The reaction is probably due to the intermediate formation of $CCl_2(CH_2CO_2Et)_2$. White needles (chloroform) or plates (hot benzene). V. sol. water, alcohol, and ether, less in chloroform, insol. cold benzene. By zinc-dust and acetic acid it is reduced to glutaconic acid [132°]; by sodium amalgam to glutaric acid. By alcoholic KOH it is converted into glutinic acid $HO_2C.C{:}C.CH_2.CO_2H$ (Burton a. Pechmann, *B.* 20, 145).

DI-CHLORO-GLUTAZINE *v.* DI-CHLORO-DI-OXY-AMIDO-PYRIDINE.

TRI-CHLORO-ISOGLYCERIC ACID *v.* TRI-CHLORO-PYRUVIC ACID.

DI-CHLORO-GLYCOCOLL *v.* DI-CHLORO-AMIDO-ACETIC ACID.

DI-CHLORO-GLYCOLLIC ACID. The dialkyl ethers $CCl_2(OR').CO_2R'$ of this acid are the primary products of the action of PCl_5 upon oxalic ethers. On distillation under ordinary atmospheric pressure they split off alkyl chlorides, and are converted into the chloro-glyoxylic ethers $Cl.CO.CO_2R'$ (Anschütz, *B.* 19, 2158).

Di-n-propyl ether $CCl_2(OPr).CO_2Pr$: (111° at 12mm.); colourless liquid. Formed by the action of PCl_5 upon mono-propyl oxalate $C_2O_2(OH)(OPr)$.

Di-isoamyl ether $CCl_2(OC_5H_{11}).CO_2C_5H_{11}$: (152° at 13mm.); colourless liquid. Formed by the action of PCl_5 upon mono-isoamyl oxalate (Anschütz a. Schönfeld, *B.* 19, 1443).

DI-CHLORO-GLYCOLLO-NITRILE $CCl_2(OH).CN$.

Methyl derivative $CCl_2(OMe)CN$. (149°). S.G. 1·39. From di-chloro-acetonitrile and NaOMe (Bauer, *A.* 229, 168). Pleasant smelling liquid, nearly insol. water, but slowly decomposed by it. V. sol. alcohol, ether, and light petroleum. Changes on keeping into a solid isomeride.

Ethyl derivative $CCl_2(OEt)CN$. (161°). S.G. $\underline{15\cdot5}$ 1·339. V.D. 153·24. Polymerises forming a white solid. [171°].

Propyl derivative $CCl_2(OPr)CN$. (183°). S.G. $\underline{15\cdot5}$ 1·238. V.D. 174.

Isobutyl derivative $CCl_2(OC_4H_9)CN$. (196°). S.G. $\underline{15\cdot5}$ 1·123.

These bodies combine with $PtCl_4$, forming compounds such as $CCl_2(OEt)CNPtCl_4$ (Bauer, *A.* 229, 182).

They are acted upon by dry HBr with formation of tri-chloro-aceto-nitrile, probably as a result of these reactions:

(i.) $CCl_2(OMe)CN + HBr$
$= MeBr + CCl_2(OH)CN$.
(ii.) $CCl_2(OH)CN = HCl + Cl.CO.CN$.
(iii.) $CCl_2(OH)CN + HCl = CCl_3.CO.NH_2$
(Bauer, *A.* 229, 192).

So also dilute H_2SO_4 converts $CCl_2(OMe)CN$ into CCl_2CO_2Me and $CCl_2(OEt)CN$ into CCl_2CO_2Et.

CHLORO-GLYOXIM $C_2H_3ClO_2N_2$ *i.e.* $CCl(NOH).CH(NOH)$. [151°]. Formed by the action of hydroxylamine on chloral-hydrate (Nägeli, *B.* 16, 499). Glistening prismatic needles. Sol. water and alcohol.

CHLORO-GLYOXYLIC ETHER $Cl.CO.CO_2Et$. *Ethoxy-oxalyl chloride.* (131°). S.G. $\underline{18}$ 1·216. V.D. 4·68 (calc. 4·71) Prepared by distilling oxalic ether with PCl_5 (V.v. Richter, *B.* 10, 2228; *C. C.* 1878, 446; *cf.* Henry, *B.* 4, 599).

Properties.—Fuming liquid; decomposed by water with formation of oxalic acid. Alcohol gives oxalic ether. Alcoholic NH_3 gives oxamic ether. Aniline forms $CO_2Et.CO.NPhH$.

Reactions.—1. *Zinc ethyl,* followed by water, forms oxy-hexoic ether $CEt_2(OH).CO_2Et$ (Henry, *B.* 5, 949).—2. With *urea* it gives ethyl oxalurate, $NH_2.CO.NH.CO.CO_2Et$ (Henry, *B.* 4, 599; Salomon, *B.* 9, 376).—3. With $HgPh_2$ it gives phenyl-glyoxylic acid (Claisen a. Morley, *B.* 11, 1596).—4. With *di-methyl-aniline* it gives di-methyl-amido-phenyl-glyoxylic acid.—5. With *di-phenyl-thiurea* dissolved in benzene it reacts vigorously, giving off CO_2 and ethyl chloride and forming aniline and a compound which is probably thio-carbanilido-thio-oxanilide $NPhH.CS.NPh.CO.CS.NPhH$ (v. Stojentin, *J. pr.* [2] 32, 2). This body melts at [231°]. It dissolves in ether, sparingly in alcohol, not at all in water. It exhibits the following *reactions*: (*a*) Warmed with alcoholic $AgNO_3$ it forms Ag_2S and di-phenyl-parabanic acid, [204°], $CO\Big<\begin{matrix}NPh-CO\\ \quad\quad\ \ | \\ NPh-CO\end{matrix}$. (*b*) Forms a red solution in aniline, which when warmed with dry alcohol and $AgNO_3$ forms oxalyl-tri-phenyl-guanidine, $C(NPh)\Big<\begin{matrix}NPh.CO\\ \quad\quad | \\ NPh.CO\end{matrix}$ [230°]. (*c*) Fuming HNO_3 forms a compound $C_{15}H_8N_4SO_5$. It melts at [235°], is insol. ether, benzene, CS_2 and light petroleum, and is readily decomposed by aqueous NaOH, *p*-nitraniline being formed. (*d*) Alcoholic NH_3 converts it into $C_{14}H_{18}N_4O_3$, a body which crystallises from alcohol in white needles, [220°], and which is itself converted by fuming HNO_3 into another body, $C_{13}H_{14}N_6O_8$, sparingly soluble in water or alcohol, [235°].—6. With *phenyl thiurea,* dissolved in boiling benzene, it acts thus: $2NH_2.CS.NPhH + ClCO.CO_2Et = NH(CS.NPh)_2C_2O_2 + NH_3 + EtCl + H_2O$. The product is oxalyl-di-phenyl-di-thio-biuret. It forms slender needles (from alcohol) [215°].—7. When warmed with *phenyl-urea* it reacts as follows: $NPhH.CO.NH_2 + Cl.CO.CO_2Et = NPhH.CO.NH.CO_2Et + CO + HCl$, and also in the following way: $NPhH.CO.NH_2 + Cl.CO.CO_2Et = NPh\Big<\begin{matrix}CO\\ C_2O_2\end{matrix}\Big>NH + ClEt + H_2O$. The chief products are, therefore, phenyl-allophanic ether, which forms needles (from alcohol), [120°], and phenyl-parabanic acid, which forms plates (from alcohol), [208°].—8. With *di-phenyl-urea* it forms di-phenyl-parabanic acid, [204°]: $NPhH.CO.NPhH + Cl.CO.CO_2Et = NPh\Big<\begin{matrix}CO\\ C_2O_2\end{matrix}\Big>NPh + EtCl + H_2O$.—9. With *tri-phenyl-guanidine* it forms carbonyl-tri-phenyl-guanidine:
$(NPhH)_2:C:NPh + 2Cl.CO.CO_2Et$
$= NPh:C\Big<\begin{matrix}NPh\\ NPh\end{matrix}\Big>CO,HCl + HCl + CO + Et_2C_2O_4$.

The hydrochloride of this base forms concentric needles (from alcohol), [190°]; its nitrate, B',HNO_3, forms octahedra (from alcohol), [185°]. By means of fuming nitric acid white needles of the formula $C_{15}H_{12}N_2O_8,\frac{1}{2}aq$, may be got (M. v Stojentin, *J. pr.* [2] 32, 1).

CHLORO-GUANIDINE CH_4ClN_3. From guanidine carbonate and chlorine (Kamenski, *B.* 11, 1602). Pale yellow crystalline powder. Detonates about 147°.

CHLORO-HEPTANE *v.* HEPTYL CHLORIDE.

Di-chloro-heptane $C_7H_{14}Cl_2$ *i.e.* $Pr.CH_2.CH_2.CH_2.CHCl_2$. *Heptylidene chloride.* (191° cor.). From œnanthol and PCl_5 (Limpricht, *A.* 103, 80). Converted by Na into heptylene. Alcoholic KOH gives chloro-heptylene.

Di-chloro-heptane $C_7H_{14}Cl_2$ *i.e.* Pr_2CCl_2. (181°). From di-*n*-propyl ketone and PCl_5 (Tavildaroff, *B.* 9, 1442).

Di-chloro-heptane Pr_2CCl_2. From di-isopropyl ketone and PCl_5 (Henry, *B.* 8, 400). Splits up into HCl and $C_7H_{13}Cl$ on distillation. Alcoholic KOH gives C_7H_{12} (78°).

CHLORO-HEPTENOIC ACID $C_7H_{11}ClO_2$. From propyl-aceto-acetic ether and PCl_5 (Demarçay, *B.* 10, 1178). Oil.

Chloro-heptenoic acid $C_7H_{11}ClO_2$. From iso-propyl-aceto-acetic acid and PCl_5 (D.). Oil.

CHLORO-HEPTYL ALCOHOL $C_7H_{15}ClO$. (207°). S.G. ^{0} 1·014. From octylene and HClO (De Clermont, *Z.* 1870, 411).

CHLORO-HEXANE *v.* Hexyl chloride.

Di-chloro-hexane $C_6H_{12}Cl_2$ *i.e.* $CH_3.CHCl.CH_2.CH_2.CHCl.CH_3$. (170°–180°). From diallyl and fuming HClAq (Wurtz, *A. Ch.* [4] 3, 161).

Di-chloro-hexane $C_6H_{12}Cl_2$. (c. 182°). S.G. ^{20} 1·087. From the hexane of petroleum by chlorination (Cahours, *A. Ch.* [4] 1, 5).

Di-chloro-hexane $C_6H_{12}Cl_2$. (160°). Formed by chlorination of diisopropyl (Schorlemmer, *A.* 144, 187; Silva, *B.* 6, 36; 7, 953).

Di-chloro-hexane $C_6H_{12}Cl_2$ *i.e.* $(CH_3)_2.CCl.CCl.(CH_3)_2$. [160°]. From pinacone and $POCl_3$ (Friedel a. Silva, *B.* 6, 35). Crystalline.

Di-chloro-hexane $(CH_3)_3C.CCl_2.CH_3$. [151°]. From pinacoline and PCl_5 (Favorsky, *J. pr.* [2] 37, 393). Very volatile crystals. Gives with alcoholic potash $CMe_3.C{:}CH$.

Di-chloro-hexane $C_6H_{12}Cl_2$ *i.e.* $CH_3.CHCl.CHCl.CH_2.CH_2.CH_3$. (c. 164°). S.G. ^{11} 1·053. From chloro-ethyl-propyl-carbinol and PCl_5 (Henry, *Bl.* [2] 41, 363). Alcoholic KOH gives $C_6H_{11}Cl$ (122°).

Tri-chloro-hexane $C_6H_{11}Cl_3$. (c. 217°). S.G. ^{21} 1·193. Formed by chlorinating *n*-hexane (Cahours, *J.* 1863, 525).

Hexa-chloro-hexane $C_6H_6Cl_6$. (c. 288°). S.G. ^{20} 1·598. From *n*-hexane and Cl (C.).

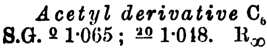
CHLORO-HEXENOIC ACID *v.* Chloro-ethyl crotonic acid.

Chloro-hexenoic acid $C_6H_9ClO_2$. [64°]. From di-methyl-aceto-acetic ether and PCl_5 (D.).

CHLORO-HEXENYL ALCOHOL $C_6H_{11}ClO$. *Allyl-chloro-propyl carbinol* (c. 185°). S.G. ^{20} 1·032. R_∞ 58·3. From epichlorhydrin (150 g.), allyl iodide (273 g.), and zinc at 0°; the product being treated with water (Lopatkin, *J. pr.* [2] 30, 390). Oil. Oxidation gives chloro-oxy-valeric acid.

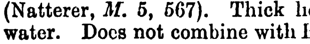
Acetyl derivative $C_6H_{11}ClOAc$. (c. 205°). S.G. ^{0} 1·065; ^{20} 1·018. R_∞ 75·1.

Chloro-hexenyl alcohol $C_6H_{11}ClO$ *i.e.*



$CH_2{<}\begin{matrix}CH_2\\CHMe\end{matrix}{>}CCl.CH_2OH$ (?). *Chloro-methyl-tetra-methylene-carbinol.* (c. 167°). From the following di-chloro-hexenyl alcohol by treatment with iron and acetic acid (Natterer, *M.* 5, 579). Liquid, sl. sol. water. Does not combine with Br. Gives with PCl_5 a liquid $C_6H_9Cl_3$ (100° at 20 mm.).

Di-chloro-hexenyl alcohol $C_6H_{10}Cl_2O$ *i.e.*



$CH_2{<}\begin{matrix}CH_2\\CH(CH_2Cl)\end{matrix}{>}CCl.CH_2OH$ (?). (c. 117°) at 20 mm. From $\alpha\gamma$-di-chloro-crotonic aldehyde by successive treatment with $ZnEt_2$ and water (Natterer, *M.* 5, 567). Thick liquid; v. sl. sol. water. Does not combine with Br.

Acetyl derivative $C_6H_9Cl_2OAc$. (123°) at 20 mm. Converted by AgOAc at 110° into $C_6H_9Cl(OAc)_2$ (140° at 20 mm.).

CHLORO-HEXINENE *v.* Hexinyl chloride.

Tetra-chloro-hexinene $C_6H_6Cl_4$. Formed by the action of PCl_5 on mannite or dulcite (Bell, *B.* 12, 1273).

CHLORO-HEXOIC ACID $C_6H_{11}ClO_2$ *i.e.* $CEt_2Cl.CO_2H$. *Chloro-caproic acid.*

Ethyl ether EtA′. From PCl_5 and the oxy-acid (derived from oxalic ether) (Markownikoff, *B.* 6, 1175). On distillation it gives HCl and hexenoic ether; sodium amalgam gives hexoic (di-ethyl-acetic) acid.

γ-Chloro-isohexoic acid $Me_2CCl.CH_2.CH_2.CO_2H$.

Ethyl ether A′Et: (88° at 12 mm.). Formed by saturating an absolute alcoholic solution of isocaprolactone (the lactone of oxy-hexoic acid) with HCl. On distillation it evolves HCl and yields pyroterebic ether (Bredt, *B.* 19, 514).

Tri-chloro-hexoic acid $C_6H_9Cl_3O_2$. [64°]. Formed by oxidation of the corresponding aldehyde by HNO_3 (Pinner, *B.* 10, 1052). Zinc and HCl convert it into hexenoic acid.

TRI-CHLORO-HEXOIC ALDEHYDE $C_6H_9Cl_3O$. *Hexyl-chloral.* (213°). Occurs among the products of the chlorination of aldehyde (Pinner, *B.* 10, 1052). Potash splits it up into formic acid, $C_5H_8Cl_2$, and HCl.

CHLORO-HEXYL ALCOHOL $C_6H_{13}ClO$ *i.e.* $CH_3.CH_2.CH_2.CHCl.CH(OH).CH_3$. *Methylchloro-butyl carbinol.* (170°). S.G. ^{11} 1·018 From hexylene and HOCl (Domac, *M.* 2, 319). Iron and HOAc give *sec*-hexyl alcohol.

Chloro-hexyl alcohol $C_6H_{13}ClO$ *i.e.* $CH_3.CH_2.CH_2.CH(OH).CHCl.CH_3$ (?). *Hexylene chlorhydrin.* (171°). S.G. ^{11} 1·011. From hexylene oxide and HCl (Henry, *C. R.* 97, 260). Oil, with sweetish taste.

Acetyl derivative $C_6H_{12}Cl.OAc$. (189°). S.G. ^{6} 1·04.

δ-Chloro-*n*-hexyl-alcohol $CH_3.CHCl.CH_2.CH_2.CH_2.CH_2.OH$ (?). *Hexylene δ-chlorhydrin.* Formed by heating the glycol with HCl (Lipp, *B.* 18, 3283). Colourless liquid of peculiar smell. Heavier than water, in which it is insoluble. By further heating with HCl it is converted into the di-chloride.

Chloro-hexyl alcohol $C_6H_{13}ClO$ *i.e.* $CMe_2Cl.CMe_2.OH$. [55°]. From $CMe_2{:}CMe_2$ and HOCl (Eltekoff, *J. R.* 14, 390). Needles, smelling of camphor. Aqueous KOH forms pinacone; solid KOH gives hexylene oxide.

Di-chloro-hexyl alcohol $C_6H_{12}Cl_2O$. (208°). S.G. ^{12} 1·4. From hexenyl alcohol and chlorine (Destrem, *A. Ch.* [5] 27, 58).

CHLORO-HEXYLENE *v.* Hexenyl chloride.

Di-chloro-hexylene $C_6H_{10}Cl_2$ *i. e.* $CH_3.CCl_2.CH_2.CH_2.CH{:}CH_2$. *Allyl-chloracetol.* (150°). From methyl butenyl ketone and PCl_5 (Henry, *C. R.* 87, 171). Heavy oil. Hot water reconverts it into the ketone. Alcoholic KOH gives C_6H_9Cl.

Di-chloro-hexylene. $C_6H_{10}Cl_2$. From mesityl oxide and PCl_5. Smells like turpentine and resinifies in the air. Distillation over lime converts it into C_6H_9Cl (130°) (Baeyer, *A.* 140, 298).

Penta-chloro-hexylene $C_6H_7Cl_5$. [102°]. From quercite by treatment with HCl. Needles (Prunier, *A. Ch.* [5] 15, 1).

***m*-CHLORO-HIPPURIC ACID** $C_9H_8ClNO_3$ *i e.* [3:1] $C_6H_4Cl.CO.NH.CH_2.CO_2H$. From hippuric acid, $KClO_3$, and HCl (Otto, *A.* 122, 129). Found in the urine after taking *m*-chloro-benzoic acid (Græbe a. Schultzen, *A.* 142, 346). Viscid mass, sol. boiling water, mixes with alcohol and ether. Its alkaline solution turns brown in air. Boiling conc. HCl gives glycocoll and m-chloro-benzoic acid.

Salts.—$NaHA'_2\frac{1}{2}aq$: stellate groups of needles.—CaA'_2: scales (from alcohol).—PbA'_2. [100°].

Di-chloro-hippuric acid $C_9H_7Cl_2NO_3$ *i.e.* [1:2:4] $C_6H_3Cl_2.CO.NH.CH_2.CO_2H$. Formed together with the preceding by chlorinating hippuric acid with HCl, and $KClO_4$ (O.). Soft, semi-crystalline mass; less sol. water than the preceding acid. Conc. HCl splits it up into glycocoll and (1, 2, 4)-di-chloro-benzoic acid.

Salts.—$NaA'aq$: soft warty crystals.—$CaA'_2 5aq$ (from hot water).—$CaA'_2 9aq$.—$CaA'_2 10aq$ (from cold water).—$BaA'_2 3aq$.—$PbA'_2 4aq$.—$(PbA'_2)_2PbO$.—AgA': cauliflower-like masses (from hot water).

Ethyl ether EtA'. Oil.

CHLORHYDRIN *v.* Glycerin.

Dichlorhydrin *v.* Di-chloro-propyl alcohol and Epichlorhydrin.

Trichlorhydrin *v.* Tri-chloro-propane.

CHLORO-HYDRACRYLIC ACID *v.* Chloro-oxy-propionic acid.

CHLORO-HYDRO-ATROPIC ACID *v.* Chloro-phenyl-propionic acid.

CHLORO-HYDRO-CINNAMIC ACID *v.* Chloro-phenyl-propionic acid.

DI-CHLORO-HYDROCŒRULIGNON *v.* *Tetra-methyl*-di-chloro-hexa-oxy-diphenyl.

CHLORO-HYDRONAPHTHOQUINONE $C_{10}H_7ClO_2$ *i. e.* $C_{10}H_5Cl(OH)_2$ [117°]. From chloro-(β)-naphthoquinone in acetic acid by passing in SO_2 (Zincke, *B.* 19, 2498). Needles (from water).

Di-chloro-hydronaphthoquinone $C_{10}H_6Cl_2O_2$ *i.e.* $C_{10}H_4Cl_2(OH)_2$. [125°]. From di-chloro-(β)-naphthoquinone and SO_2 (Zincke, *B.* 19, 2500). Slender needles.

Di-chloro-(α)-hydronaphthoquinone $C_{10}H_4Cl_2(OH)_2$. [135° uncor.]. Formed by shaking an ethereal solution of di-chloro-(α)-naphthoquinone with aqueous $SnCl_2$ till decolourised. Long colourless needles. V. sol. alcohol, ether, &c., insol. water. By air oxidation it is converted into the quinhydrone $C_{20}H_{10}Cl_4O_4$, which forms long violet-brown needles [250° uncor.] (Claus, *B.* 19, 1144; *cf.* Græbe, *A.* 149, 6).

Di-acetyl derivative $C_{10}H_4Cl_2(OAc)_2$. [236°].

CHLORO-HYDROQUINONE $C_6H_3Cl(OH)_2$. [106°]. (263°). Prepared by boiling quinone with HCl (Levy a. Schultz, *B.* 13, 1427; *A.* 210, 137; *cf.* Wöhler, *A.* 51, 155; Wichelhaus, *B.* 12, 1504). Also from chloro-quinone and SO_2 (Städeler, *A.* 69, 307). Monoclinic crystals, $a:b:c = 2{\cdot}77:1:2{\cdot}31$; $\beta = 62° 3'$. V. e. sol. water and alcohol, sl. sol. chloroform. On oxidation it gives chloroquinone. Heated with phthalic anhydride it produces a chlorinated quinizarine which is soluble in caustic soda with a blue colour. Combines with aniline with formation of $C_6H_3Cl(OH)_2 2NH_2Ph$ [92°] which crystallises from hot water in glittering plates (Niemeyer, *A.* 228, 322). With p-toluidine it forms a compound melting at 90°. These compounds are not decomposed by crystallising from hot benzene.

Di-acetyl derivative $C_6H_3Cl(OAc)_2$. [72°] (L. a. S.); [99°] (Scheid, *A.* 218, 216). Transparent prisms. Sol alcohol.

Di-benzoyl derivative $C_6H_3Cl(OBz)_2$. [130°]. Long needles. Easily soluble in hot alcohol, sparingly in cold.

(α)-Di-chloro-hydroquinone $C_6H_2Cl_2(OH)_2$ [2:5:4:1]. [166°] (L. a. S.); [172°] (Krafft, *B.* 10, 800). Prepared by boiling chloro-quinone with HCl; or by passing dry HCl into a solution of chloroquinone in chloroform (Levy a. Schultz, *B.* 13, 1428; *A.* 210, 148). Formed also by reducing (α)-di-chloro-quinone [159°] with aqueous SO_2 (Stadeler, *A.* 69, 312). Long needles (from boiling water). May be sublimed. On oxidation it gives (α)-dichloro-quinone. Combines with aniline forming $C_6H_2Cl_2(OH)_2 2NH_2Ph$ [113°], which crystallises in needles (from water), tables, or prisms (from benzene). The compound with p-toluidine melts at 115° (Niemeyer, *A.* 228, 328).

Di-acetyl derivative $C_6H_2Cl_2(OAc)_2$. [141°]. Formed by the action of acetyl chloride on quinone or chloro-quinone. Monoclinic crystals (Schulz, *B.* 15, 653; *A.* 210, 148) $a:b:c = 2{\cdot}9:1:1{\cdot}13$; $\beta = 72° 40'$.

Di-benzoyl derivative $C_6H_2Cl_2(OBz)_2$. [185°]. Woolly needles, sol. benzene, insol. water.

(β)-Di-chloro-hydro-quinone $C_6H_2Cl_2(OH)_2$ [2:6:4:1]. [158°]. Formed by reduction of the corresponding quinone [120°] (Faust, *A.* 149, 155). Yellowish laminæ (from dilute alcohol). Forms with p-toluidine a compound melting at 73°.

Di-acetyl derivative $C_6H_2Cl_2(OAc)_2$ [67°]; fine needles.

Di-benzoyl derivative $C_6H_2Cl_2(OBz)_2$ [105°]; colourless needles (Levy, *B.* 16, 1445).

Di-methyl ether $C_6H_2Cl_2(OMe)_2$. [126°]. Formed by chlorinating di-methyl-hydroquinone (Habermann, *B.* 11, 1034). Small needles; may be sublimed.

Di-isobutyl ether $C_6H_2Cl_2(OCH_2Pr)_2$ (Schubert, *M.* 3, 682).

Tri-chloro-hydroquinone $C_6HCl_3(OH)_2$. [134°]. Prepared, together with tetrachlorohydroquinone, by boiling (α)- or (β)-dichloroquinone with HCl, and separated from tetra-chloro-hydroquinone by solution in water (Levy a. Schultz, *B.* 13, 1429; *A.* 210, 153). Formed also by reducing tri-chloro-quinone with SO_2 (Städeler, *A.* 69, 321; Stenhouse, *A. Suppl.* 6, 214; Græbe, *A.* 146, 25), and by oxidising benzene with $KClO_3$ and H_2SO_4 (Krafft, *B.* 10, 797; Carius, *A.* 142, 129). Flattened prisms. Its alkaline solutions turn brown in the air, ultimately forming di-chloro-di-oxy-quinone (chloranilic acid). It forms two compounds with aniline: $C_6HCl_3(OH)_2$, NH_2Ph [60°], crystallising in small needles, and $C_6HCl_3(OH)_2$, $2NH_2Ph$ [67°], crystallising in trimetric tables. With phthalic anhydride it does not produce chlorinated quinizarine.

Di-acetyl derivative $C_6HCl_3(OAc)_2$. [153°]. Needles.

Di-benzoyl derivative $C_6HCl_3(OBz)_2$. [174°]. Needles.

Di-ethyl ether $C_6HCl_3(OEt)_2$. [68·5°]. Long needles.

Tetra-chloro-hydroquinone $C_6Cl_4(OH)_2$. [232°] (Sutkowski, *B.* 19, 2316).

Prepared by boiling (β)-dichloro quinone or tri-chloro-quinone with HCl (Levy a. Schultz, *B.* 13, 1429; *A.* 210, 255), or by passing HCl into a solution of tri-chloro-quinone in acetic acid (Niemeyer, *A.* 228, 324). Formed also by boiling tetra-chloro-quinone with $SnCl_2$, with HClAq, with HBrAq, or with aqueous SO_2. Monoclinic pyramids; $a:b:c = 3{\cdot}0:1:2{\cdot}58$; $\beta = 76°\,34'$. May be sublimed. Insol. water, v. sl. sol. benzene, v. sol. alcohol and ether. Reduces silver solution. PCl_5 converts it into C_6Cl_6. A conc. solution in hot potash deposits, on cooling, prisms of $C_6Cl_4(OK)_2$. A solution of this salt exposed to air forms $C_6Cl_2O_2(OK)_2$. Combines with aniline, forming $C_6Cl_4(OH)_2NH_2Ph$ [115°].

Di-acetyl derivative $C_6Cl_4(OAc)_2$. [245°].

Di-benzoyl derivative $C_6Cl_4(OBz)_2$. [233°]. Sol. benzene, sl. sol alcohol.

Di-methyl ether $C_6Cl_4(OMe)_2$. [154°]. From di-methyl-hydroquinone and Cl (Habermann, *B.* 11, 1035). Needles.

Di-ethyl ether $C_6Cl_4(OEt)_2$. [112°]. From tetra-chloro-hydroquinone, KOH, EtI, and alcohol at 140° (Græbe, *A.* 146, 19). Needles.

Methyl ethyl ether $C_6Cl_4(OMe)(OEt)$. [101°]. From $C_6H_4(OMe)(OEt)$ and Cl (Fiala, *M.* 6, 912).

Di-isobutyl ether $C_6Cl_4(OCH_2Pr)_2$ (Schubert, *M.* 3, 682).

DI-*p*-CHLORO-HYDROQUINONE-DI-CARBOXYLIC ETHER *v.* DI-*p*-CHLORO-DI-*p*-OXY-TEREPHTHALIC ETHER.

DI-CHLORO-HYDROQUINONE DI-SULPHONIC ACID
$C_6H_4Cl_2S_2O_8$ *i.e.* $C_6Cl_2(OH)_2(SO_3H)_2$. From tetra-chloro-quinone and aqueous $KHSO_4$ (Hesse, *A.* 114, 324; Greiff, *C. C.* 1863, 1041). The free acid is unstable. It gives an indigo-blue colour with Fe_2Cl_6. Alkaline solutions are oxidised by air to euthiochronic acid.—$K_2A''2aq.$—$(NH_4)_2A''2aq.$

Tri-chloro-hydroquinone sulphonic acid
$C_6H_3Cl_3SO_5$ *i.e.* $C_6Cl_3(OH)_2SO_3H$. Formed, together with euthiochronic acid, by dissolving tri-chloro-quinone in warm aqueous K_2SO_3 (Græbe, *A.* 146, 55). Deliquescent needles. Fe_2Cl_6 gives a blue colour.—KA′aq. Alkaline solutions are oxidised in air to

$$C_6Cl(OK)_2O_2(SO_3K).$$

CHLORO-HYDRO-THYMOQUINONE
$C_{10}H_{13}ClO_2$ *i.e.* $C_6HCl(C_3H_7)(CH_3)(OH)_2$ [2:6:3:4:1]. [70°]. From thymoquinone and conc. aqueous HCl at 0° (Schniter, *B.* 20, 1317). Silky needles.

Di-acetyl derivative $C_{10}H_{11}Cl(OAc)_2$. [88°]. Formed by the action of acetyl chloride on thymoquinone. Large crystals.

Di-benzoyl derivative [118°]. Colourless needles (Schulz, *B.* 15, 657).

Di-chloro-hydrothymoquinone

Di-benzoyl derivative $C_{10}H_{10}Cl_2(OBz)_2$. [191°]. Formed by the action of benzoyl chloride on thymoquinone (Schulz, *B.* 15, 658). Sparingly soluble white needles.

CHLORO-HYDROTOLUQUINONE
$C_6H_2(CH_3)Cl(OH)_2$ [1:3or4:2:5]. [175° uncor.]. Formed by reduction of chloro-toluquinone [90°] with SO_2. Long colourless needles. Sublimable and volatile with steam (Claus a. Schweitzer, *B.* 19, 929).

Chloro-hydro-toluquinone $C_6H_2MeCl(OH)_2$. [175°]. Obtained by the action of cold conc. HCl upon toluquinone. White plates or needles. V. sol. alcohol, ether, and hot water, sl. sol. ligroïn (Schniter, *B.* 20, 2283).

Di-chloro-hydro-toluquinone
$C_6HMeCl_2(OH)_2$. [121°]. Formed by the action of HCl upon chloro-toluquinone. Not volatile with steam (Schniter, *B.* 20, 2288). Formed also by reducing di-chloro-toluquinone obtained from di-chlorinated *o*-cresol [54°] (Claus a. Schweitzer, *B.* 19, 937; *cf.* Southworth, *A.* 168, 274). Feathery crystals (from water). May be sublimed.

Di-chloro-hydrotoluquinone
$C_6H(CH_3)Cl_2(OH)_2$. [171° uncor.]. Formed by reduction of di-chloro-toluquinone [103°] (from di-chloro-*m*-cresol) with SO_2. Colourless needles. V. e. sol. alcohol, ether, &c., sol. hot water, sl. sol. cold (Claus a. Schweitzer, *B.* 19, 931).

Acetyl derivative $C_6HMeCl_2(OAc)_2$. [124°] (Southworth).

Tri-chloro-hydrotoluquinone $C_6MeCl_3(OH)_2$. [212°]. From tri-chloro-toluquinone and aqueous SO_2 at 100° (Southworth; Borgmann, *A.* 152, 251; Hayduck, *A.* 172, 211; Claus a. Riemann, *B.* 16, 1603). Needles. Volatile with steam. Turns green in moist air.

Di-acetyl derivative $C_6MeCl_3(OAc)_2$. [114°].

Di-ethyl ether $C_6MeCl_3(OEt)_2$. [107°].

Tetra-chloro-hydrotoluquinone $C_7H_4Cl_4O_2$. From tetra-chloro-toluquinone and SO_2 (Bräuninger, *A.* 185, 353). Needles (by sublimation).

CHLORO-HYDROTOLUQUINONE DI-SULPHONIC ACID $C_6MeCl(OH)_2(SO_3H)_2$. From tri-chloro-toluquinone and conc. aqueous $KHSO_3$ (Borgmann, *A.* 152, 255).—KA′: laminæ.

CHLORO-HYDROXYLOQUINONE
$C_6HClMe_2(OH)_2$ [*x*:1:4:2:5]. [147°]. Formed, together with the di-chloro- compound, by treating xyloquinone (phlorone) with conc. HCl (Carstanjen, *J. pr.* [2] 23, 421). Needles. Fe_2Cl_6 colours its aqueous solution violet.

Di-chloro-hydroxyloquinone $C_6Cl_2Me_2(OH)_2$. [180°]. Formed as above (C.) or by reducing di-chloro-xyloquinone with aqueous SO_2 (Rad, *A.* 151, 164). Coloured violet by Fe_2Cl_6.

DI-CHLORO-ICOSYLENE $C_{20}H_{34}Cl_2$. S.G. $\frac{24}{}$ 1·013. From $C_{20}H_{38}$ and Cl (Lippmann a. Hawliczek, *B.* 12, 69).

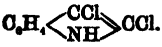
CHLOROIMIDO-CARBONIC ACID $ClN:C(OH)_2$.

Methyl ether $ClN.C(OMe)_2$. [20°]. Formed by leading chlorine into a cooled solution of 80 pts. NaOH and 80 pts. KCN (96–98 p.c.) in 150 pts. of methyl alcohol. White crystalline solid. Its reactions are the same as those of the ethyl ether.

Ethyl ether $ClN:C(OEt)_2$. [39°]. Formed by leading chlorine into a cooled solution of 80 pts. NaOH and 80 pts. KCN in 200 pts. of ethyl alcohol; the yield is 50 pts. of the pure product. Large colourless prisms. V. sol. alcohol and ether, insol. water. Rotates on water. Decomposes on distillation. Heated with aqueous H_2S it yields carbonic ether NH_4Cl and S. By dilute acids it is split up into carbonic ether, chloride of nitrogen and NH_3. From HI it liberates iodine. By warming with a solution of potassium arsenite it is reduced to imido-carbonic ether $HN:C(OEt)_2$ (Sandmeyer, *B.* 19, 862).

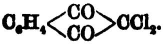
TETRA-CHLORO-INDIGO $C_{16}H_6Cl_4N_2O_2$. Very analogous to ordinary indigo. Obtained by the action of acetone and NaOH on di-chloro-nitro-benzoic aldehyde (Gnehm, *B.* 17, 752).

DI-CHLOR-INDOLE $C_8H_5Cl_2N$ *i.e.*



$C_6H_4\left<\begin{matrix}CCl\\NH\end{matrix}\right>CCl$. [104°]. *Chlor-oxindole-chloride*. From oxindole and PCl_5. Crystalline mass smelling like fæces. Colourless laminæ (from hot water), v. e. sol. alcohol, ether, and benzene. Sol. alkalis. Can be methylated (Baeyer, *B.* 12, 456; 15, 786).

DI-CHLORO-INDONAPHTHOQUINONE



$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>CCl_2$. [125°].

Formation.—Tetrachloro-(β)-naphthoquinone is dissolved in Na_2CO_3Aq, HOAc is added and afterwards HCl and chromic acid, the mixture being gently warmed (Zincke, *B.* 21, 499).

Properties.—Plates (from dilute alcohol or HOAc).

DI-CHLORO-IODHYDRIN *v.* DI-CHLORO-IODO-PROPANE.

αβ- or βα-CHLORO-IODO-ACRYLIC ACID CHI:CCl.CO_2H or CHCl:CI.CO_2H. [72°]. Formed by boiling propiolic acid with an ethereal solution of ClI (Stolz, *B.* 19, 538). Pearly crystals. Easily soluble in all solvents.

Chloro-di-iodo-acrylic acid $C_3HO_2ClI_2$ *i.e.* CI_2:CCl.CO_2H(?). [143°]. Formed by boiling iodo-propiolic acid with an ethereal solution of ClI (Stolz, *B.* 19, 538). Colourless glistening plates. Sparingly soluble in ligroin and cold water, more easily in alcohol and ether.

o-CHLORO-IODO-BENZENE C_6H_4ClI [2:1]. (above 233°) (Korner); (230°) (B. a. K.). S.G. $\frac{24{\cdot}5}{}$ 1·928. From *o*-chloro-aniline by displacing NH_2 by I through the diazo- reaction (Korner, *G.* 4, 343; Beilstein a. Kurbatoff, *A.* 176, 33).

p-Chloro-iodo-benzene C_6H_4ClI [4:1]. [56°]. (227°). From *p*-chloro-aniline by displacing NH_2 by I; or from *p*-iodo-aniline by displacing NH_2 by Cl.

CHLOR-IODO-BENZOIC ACID $C_6H_3ClI.CO_2H$ [210°]. Formed by the action of an alcoholic solution of iodine upon chloro-salicylic acid [172°] (Smith a. Knerr, *Am.* 8, 95). Curved needles. Sol. boiling water.

Salts.—BaA'_2. Arborescent crystals.

CHLORO-IODO-ETHANE C_2H_4ClI *i.e.* $CH_2Cl.CH_2I$. *Ethylene chloro-iodide.* (140°) (Thorpe, *C. J.* 37, 189). S.G. $\frac{0}{}$ 2·151 (Simpson); $\frac{0}{}$ 2·164 (Th.). Formed by the action of ICl on ethylene or ethylene iodide (Maxwell Simpson, *Pr.* 11, 590; *A.* 125, 101; 127, 372; *Suppl.* 6, 254).

Reactions.—1. Alcoholic KOH gives C_2H_3Cl. 2. Moist Ag_2O gives glycol. — 3. *Zinc* and H_2SO_4 gives ethylene.—4. *Silver* forms ethylene and ethylene chloride (Friedel a. Silva, *Bl.* [2] 17, 242).—5. Conc. HI forms, on heating, C_2H_4 and $C_2H_4I_2$.—6. *Ammonia* forms ethylene-diamine (Engel, *Bl.* [2] 48, 96).

Chloro-iodo-ethane $CH_3.CHICl$. *Ethylidene chloroiodide.* (118°). S.G. $\frac{12}{}$ 2·054.

Formation.—Iodine (26 g.) is suspended in water (120 g.) and saturated with chlorine in the cold. The chloride of iodine is then shaken with ethylidene iodide, the product washed with dilute KOH and distilled.

Preparation.—Al_2I_6 (8 g.) is dissolved in CS_2 (24 g.) and slowly added to ethylidene chloride (6 g.) dissolved in CS_2 (6 g.) and kept at 0° The product is treated as above (Maxwell Simpson, *Pr.* 27, 424).

Di-chloro-iodo-ethane $C_2H_3Cl_2I$. (172°). S.G. $\frac{0}{}$ 2·219. From C_2H_3Cl and ICl (Henry, *C. R.* 98, 518). Alcoholic KOH gives CH_2:CCl_2 (37°).

CHLORO-IODO-ETHYLENE C_2H_2ICl. *Acetylene chloro-iodide.* (119° i. V.) (Plimpton); (115°) (Sabanejeff). S.G. $\frac{0}{}$ 2·230 (P.); $\frac{0}{}$ 2·154 (S.); $\frac{19{\cdot}5}{}$ 2·118 (S.). Formed by passing acetylene into a solution of ICl in HCl (Plimpton, *C. J.* 41, 392) or in ether (McGowan, *Pr. E.* 9, 589).

Preparation.—Chlorine is passed into water (6 pts.) containing iodine (1 pt.). The liquid is poured off from undissolved iodine, and acetylene is then passed in (Sabanejeff, *A.* 216, 264).

Reactions.—1. *Zinc* and alcohol gives off acetylene.—2. Alcoholic $AgNO_3$ forms needles of a double compound.—3. Heated with 50 vols. of *water* at 150°, it is dissolved in 6 days the products being HI, C_2HCl and chloro-ethylene oxide C_2H_3ClO (*q. v.*).—4. Alcoholic KOH gives off a gas that decomposes in air (chloro- or iodo-acetylene).

Chloro-iodo-ethylene CH_2:CClI. (101°). S.G. $\frac{0}{}$ 2·143. From chloro-bromo-iodo-ethane and alcoholic KOH (Henry, *C. R.* 98, 741). Oil; turns purple in air and light, absorbing oxygen

DI-CHLORO-TETRA-IODO-FLUORESCEIN. *Hydrate.* $C_{20}H_8Cl_2I_4O_6$. Formed by adding a solution of iodine in dilute KOH to an alkaline solution of di-chloro-fluorescein and acidifying (Le Royer, *A.* 238, 359). The alkaline salts are used as dyes ('Rose Bengale').

CHLORO-IODO-METHANE CH_2ICl. (109°). S.G. $\frac{20}{}$ 2·49. From IHg.CH_2Cl and I_2 (Sakurai, *C. J.* 41, 362).

Di-chloro-iodo-methane $CHCl_2I$. (131°). S.G. $\frac{0}{}$ 2·454. *Chloriodoform.* A liquid formed by the action of $HgCl_2$ or PCl_5 on iodoform (Serullas, *A. Ch.* [2] 25, 314; 39, 225; Mitscherlich, *P.* 11, 164; Bouchardat, *A.* 22, 229; Schlagdenhauffen, *J. Ph.* [3] 30, 401; Borodin, *A.* 126, 239).

Di-chloro-di-iodo-methane CCl_2I_2. [85°]. From CHI_3 and $HgCl_2$ (Borodin, *A.* 126, 239). From CH_2Cl_2 and IBr (Höland, *A.* 240, 234). Glittering scales, with pungent odour. Turned brown by light, alcohol, and ether.

CHLORO-IODO-METHYL-PYRIDINE C_6H_5ClIN. [111°]. *Chloro-iodo-picoline.* From chloro-(α)-picoline, [21°], by digesting with I and NaOH. Prisms, apparently trimetric (Ost, *J. pr.* [2] 27, 257).

CHLORO-IODO-NITRO-BENZENE $C_6H_3ClI(NO_2)$ [1:3:4] [63°]. From the corresponding chloro-nitro-aniline [123°] by displacing NH_2 by I through the diazo- reaction (Körner, *G.* 4, 381). Prisms (from ether-alcohol); volatile with steam; sl. sol. cold alcohol.

Chloro-iodo-nitro-benzene $C_6H_3ClI(NO_2)$ [1:4:3]. [63°]. From chloro-nitro-aniline [116°] by the diazo- reaction (K.). Spherical groups of needles (from hot alcohol).

CHLORO-IODO-o-OXY-BENZOIC ACID $C_6H_2(OH)ClI(CO_2H)$ [3:*x*:5:1]. *Chlor-iodo-salicylic acid.* [224°]. Prepared by heating chloro-salicylic acid with iodine and HgO in alcoholic solution (Smith a. Knerr, *Am.* 8, 95). Colourless needles (from dilute alcohol). V. sl. sol. hot water. Gives a violet colour with Fe_2Cl_6.

Salts. $BaA'_2 4\frac{1}{2}aq$: pink needles; m. sol. water.—$NaA' 2aq$: flat needles. $CaA'_2 5aq$: pink needles; sol. water.—$MgA'_2 5\frac{1}{2}aq$: pink leaflets; sol. hot water.—$ZnA'_2 3aq$: white needles; v. sol. hot water.

Methyl ether MeA'. [130°]. Flat needles.

Ethyl ether EtA'. White plates. V. sol. hot alcohol.

TRI-CHLORO-IODO-PHENOL $C_6HCl_3I(OH)$. [80°]. From tri-chloro-amido-phenol by diazo-reaction (Lampert, *J. pr.* [2] 33, 391). White needles (from alcohol).

Ethyl derivative $C_6HCl_3I(OEt)$. [61°].

CHLORO-IODO-PROPANE C_3H_6ClI *i.e.* $CH_3.CHCl.CH_2I$. (149°). S.G. ^{0} 1·933; ^{25} 1·889. From propylene and aqueous ICl (Maxwell Simpson, *Pr.* 12, 278; Friedel a. Silva, *A. Ch.* [2] 17, 535). Converted by $HgCl_2$ at 100° into propylene chloride. HI at 100° gives isopropyl iodide and isopropyl chloride (Sorokin, *B.* 3, 626; Silva, *C. R.* 93, 739). Alcoholic KOH gives $CH_3.CCl:CH_2$.

Chloro-iodo-propane $CH_3.CClI.CH_3$. *Chloro-iodo-acetol.* (c. 120°) at 10 mm. S.G. ^{0} 1·824. From $CH_3.CCl:CH_2$ and HI (Oppenheim, *A. Suppl.* 6, 359). Decomposed by distillation under atmospheric pressure. Moist Ag_2O gives acetone.

Di-chloro-iodo-propane $C_3H_5Cl_2I$. *Di-chloro-iodhydrin.* (c. 208°). From $C_3H_5ClI(OH)$ and PCl_5 (Henry, *B.* 4, 701).

CHLORO-IODO-PROPYL ALCOHOL $C_3H_5ClI(OH)$. *Glycerin chloroiodhydrin.* (226°). S.G. ^{10} 2·06. From epiiodhydrin and HCl; or from epichlorhydrin and HI (Reboul, *A. Suppl.* 1, 225). Conc. KOHAq gives epichlorhydrin.

CHLORO-IODO-PROPYLAMINE $C_3H_5ClI(NH_2)$. From allylamine hydrochloride and ICl (Henry, *B.* 8, 399). $B'_2H_2PtCl_6$.

CHLORO-IODO-PROPYLENE C_3H_4ClI *i.e.* $CH_2:CCl.CH_2I$. (c. 150°). S.G. ^{15} 1·913. From di-chloro-propylene and CaI_2 at 100° (v. Romburgh, *R. T. C.* 1, 233). Combines with mercury. Heated with KOH or Ag_2O it yields α-chloro-allyl alcohol. $AgNO_3$ gives α-chloro-allyl nitrate.

Chloro-iodo-propylene C_3H_4ClI *i.e.* $CHCl:CH.CH_2I$. (162°). S.G. ^{18} 1·97. Colourless liquid, with irritating odour and sharp taste. Prepared by heating dry CaI_2 with $CHCl:CH.CH_2Cl$ at 100°, or by heating dry KI or CaI_2 in excess with allylidene chloride at 100° for 24 hours. Combines with Hg forming white plates, very soluble in alcohol. With KOH it yields β-chloro-allyl alcohol (P. v. Romburgh, *R. T. C.* 1, 233).

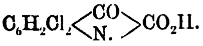
(α)-**CHLORO-IODO-TOLUENE** C_7H_6ClI. (243°). S.G. ^{17} 1·716. From (α)-chloro-nitro-toluene by reduction and displacement of NH_2 by I through the diazo- reaction (Wroblewsky, *Z.* [2] 6, 164; *A.* 168, 210). Liquid.

(β)-**Chloro-iodo-toluene** C_7H_6ClI. [10°]. (240°). S.G. $^{19·5}$ 1·770. From (β)-chloro-nitro-toluene (W.).

Chloro-iodo-toluene C_7H_6ClI. (240°). S.G. ^{42} 1·702. From chlorinated *o*-toluidine (Beilstein a. Kuhlberg, *A.* 156, 82).

CHLORO-ISATIN *v.* ISATIN.

CHLORO-ISATOIC ACID $C_8H_4ClNO_3$ *i.e.* $C_6H_3Cl\left\langle{}^{CO}_{N.}\right\rangle CO_2H$. [265°–268°]. From chloro-isatin (10 g.), CrO_3 (20 g.), and HOAc (120 g.) (Dorsch, *J. pr.* [2] 33, 49). Pearly plates (from alcohol-acetone). Insol. water, ether, and benzene. Boiling conc. HCl gives CO_2 and chloro-*o*-amido-benzoic acid. Ammonia gives CO_2 and chloro-benzamide.

Di-chloro-isatoic acid  $C_6H_2Cl_2\left\langle{}^{CO}_{N.}\right\rangle CO_2H$. [256°]. From di-chloro-isatin (10 g.), CrO_3 (15 g.), and HOAc (60 g.) (D.). Yellow prisms (from alcohol-acetone).

CHLORO-LACTIC ACID *v.* CHLORO-OXY-PROPIONIC ACID.

CHLORO-LEVULIC ACID *v.* CHLORO-ACETYL-PROPIONIC ACID.

CHLORO-LUTIDINE *v.* CHLORO-DI-METHYL-PYRIDINE.

CHLORO-MALEIC ACID $C_2ClH(CO_2H)_2$. [172°] The acid so called by Perkin and Duppa is probably chloro-fumaric acid (*q. v.*).

Formation.—Among the products of the action of ClOH on benzene (Carius, *A.* 142, 139; 155, 217; *cf.* Kekulé a. Strecker, *A.* 223, 183).

Salts.—KHA'' aq. BaA'' 5aq. Crusts.

Anhydride $C_2ClH:C_2O_3$. [0°] and [34·5°]. Formed by heating a mixture of chloro-fumaric acid and its chloride (Perkin, *C. J. Proc.* 4, 76). Dimorphous.

Di-chloro-maleic acid $C_2Cl_2(CO_2H)_2$.

Preparation. The chloride $C_2Cl_2(C_2Cl_4O)$ (see below) warmed with conc. H_2SO_4 dissolves with evolution of HCl. The crystals which separate (anhydride) are dissolved in water (becoming hydrated), the solution is extracted with ether, and the ethereal extract evaporated and placed over H_2SO_4. Hygroscopic crystals of the acid are formed. On sublimation they split up into H_2O and the anhydride, $C_2Cl_2(CO)_2O$. The acid may also be obtained by boiling its imide with potash.

Properties. Hygroscopic crystals. Changes over H_2SO_4 into the anhydride. Also by boiling with ligroin (40°), in which the anhydride dissolves, but the acid does not.

Salt. Ag_2A''. Silky needles. Explodes when heated.

Methyl ether.—Me_2A''. (225°).

Anhydride $C_2Cl_2(CO)_2O$. [120°]. Laminæ; may be sublimed. Slowly dissolves in water, changing to the acid.

Tetrachlorinated derivative of the anhydride $C_2Cl_2(C_2Cl_4O)$.

(β) Solid: [41°] (209°). **V.D. (H=1)** 251 (Theory 277). (? $C_2Cl_2(CCl_2)_2O$).

(α) Liquid: (194°–214°). V.D. (H=1) 236 (? $C_2Cl_2(CCl_3)COCl$).

Preparation.—By heating a mixture of $POCl_3$ (24 g.), succinyl chloride (8 g.) and PCl_5 (45 g.) in sealed tubes at 230°. The product is distilled and the fraction 125°–215° is treated with water. The heavy oil which separates is distilled with steam. It is chiefly liquid chloride. To get the solid isomeride, the liquid is heated with PCl_5 at 250°, the product poured into water and distilled with steam. The oily distillate is dried over $CaCl_2$ and distilled. The distillate deposits plates of the solid chloride, which may be recrystallised from alcohol of 90 per cent. (Kauder, *J. pr.* [2] 31, 2, 7).

Reactions.—1. Warm conc. H_2SO_4 converts both the solid and the liquid chloride into di-chloro-maleïc anhydride.—2. The vapour undergoes dissociation when heated strongly, hence the V.D. is rather low.—3. Water and dilute NaOH have hardly any action on the chlorides. The liquid chloride is readily decomposed by alcoholic NaOH, forming di-chloro-maleic acid.—4. Sodium amalgam reduces it in alcoholic solution to succinic acid, di-chloro-maleic anhydride being also formed.—5. The liquid chloride is violently attacked by ammonia. The solid chloride is not attacked by alcoholic ammonia below 130°. Ethylamine and aniline attack the liquid, but not the solid chloride.—6. Neither chloride is attacked by Cl or Br.—7. PCl_5 at 250° converts the liquid into the solid chloride, but breaks both up thus:

$$C_2Cl_2(C_2Cl_4O) + 3PCl_5 = 2C_2Cl_6 + 2PCl_3 + PCl_3O.$$

Imide $C_4Cl_2O_2NH$. Formed by chlorination of succinimide at 150°; or by boiling per-chloro-pyrocoll ortho-bromide with dilute acetic acid (Ciamician a. Silber, *B.* 16, 2393; 17, 553; *G.* 14, 31). Trimetric crystals, $a:b:c = \cdot 9922 : 1 : 1 \cdot 5934$. V. sol. hot water, alcohol, and ether. Heated with PCl_5 at 200° for 24 hours it is converted into the per-chloride C_4Cl_7N, which is reduced by zinc-dust and HCl to tetra-chloro-pyrrol. By heating with water it yields (*a*)-di-chloro-acrylic acid, CO_2, and NH_3.

Perchlorinated imide C_4Cl_7N. [70°-73°]. (144° at 20 mm.). White wax-like solid. V. sol. alcohol, ether, and acetic acid, nearly insol. water. Formed by heating di-chloro-maleimide with PCl_5 at 200° for 24 hours. Zinc-dust and acetic or hydrochloric acid reduce it to tetra-chloro-pyrrol (Ciamician a. Silber, *B.* 17, 551).

Phenyl-imide $C_2Cl_2{<}\begin{matrix}CO\\CO\end{matrix}{>}NPh$. [201°]. Silvery plates. Got by action of PCl_5 on phenyl-succinimide (*v.* Succinimide). HCl decomposes it into aniline and di-chloro-maleic acid.

CHLOROMALONIC ACID $C_3H_3ClO_4$ *i.e.* $CHCl:(CO_2H)_2$. [133°]. Formed by saponification of the ether by cold alcoholic KOH (Conrad a. Guthzeit, *B.* 15, 605). Prisms. Sol. water, alcohol, and ether. Heated to 180° it loses CO_2 and gives chloro-acetic acid.—A′Ag: white crystalline pp.

Diethyl ether $A''Et_2$. (222°). S.G. $\frac{20}{15}$. 1·185. Prepared by the action of chlorine on malonic ether. On saponification with KOH it gives tartronic acid (Conrad a. Bischoff, *B.* 13, 600; *A.* 209, 218). The sodium derivative reacts with [2:1] $C_6H_4(CH_2Br)_2$ with production of $C_6H_4(CH_2.CCl(CO_2Et)_2)_2$, whence alcoholic KOH gives $C_6H_4(CH:CH.CO_2H)_2$ (Perkin, *C. J.* 53, 14).

Amide $CHCl(CONH_2)_2$. [170°]. Tables, v. sol. hot water and alcohol.

CHLORO-MECONIC ACID *v.* Meconic acid.

CHLORO-MECYLENE *v.* Chloro-pentinene.

CHLORO-TRIMESIC ACID $C_6H_2Cl(CO_2H)_3$. [278°]. From oxy-trimesic acid and PCl_5 (Ost, *J. pr.* [2] 15, 308). Needles or tables (from water) (containing aq).—$Ba_3A'''_2$ 7aq: m. sol. hot water.

CHLORO-MESITYLENE $C_6H_2Cl(CH_3)_3$. (205°). Formed, together with di- and tri-chloro-mesitylene by passing chlorine into cold mesitylene (Fittig a. Hoogewerff, *A.* 150, 323; *Z.* [2] 5, 168). Fuming HNO_3 forms a di-nitro-derivative [177°].

ω-Chloro-mesitylene $C_6H_3(CH_3)_2CH_2Cl$. (215°-220°). Obtained by chlorinating mesitylene at 215° (Robinet, *C. R.* 96, 500). NaOAc gives $C_6H_3(CH_3)_2CH_2OAc$. (242°).

Di-chloro-mesitylene $C_6HCl_2(CH_3)_3$. [59°]. (244°). Formed by chlorinating cold mesitylene (F. a. H.). Prisms (from alcohol). Volatile with steam.

ω-Di-chloro-mesitylene $C_6H_3(CH_3)(CH_2Cl)_2$. [41°]. (260°). Formed by chlorinating mesitylene at 215° (R.). Needles.

Tri-chloro-mesitylene $C_6Cl_3(CH_3)_3$. [205°] (F. a. H.); [208°] (Kurbatoff, *J. R.* 1883 [1] 129). (280°). From cold mesitylene and excess of Cl (Kane, *P.* 44, 474; F. a. H.). From *o*-di-chloro-benzene, Al_2Cl_6, and MeCl at 100° (Friedel a. Crafts, *A. Ch.* [6] 10, 411). Slender needles (from alcohol). Not attacked by oxidising agents. HI (S.G. 1·9) heated with it forms mesitylene.

ω-Tri-chloro-mesitylene $C_6H_3(CH_2Cl)_3$. (c. 280°). Prepared by heating the corresponding alcohol with HCl and fractionating the crude product *in vacuo*. Has not been obtained pure. Heavy oil. Boiled with water and $PbCO_3$ it regenerates $C_6H_3(CH_2OH)_3$ (Colson, *A. Ch.* [6] 6, 97).

CHLORO-MESITYLENIC ACID $C_6H_2Cl(CH_3)_2(CO_2H)$ [4·3:5:1]. From chloro-mesitylene and dilute HNO_3 (Fittig a. Hoogewerff, *A.* 150, 325). Monoclinic prisms (from alcohol). Turns brown above 200° without melting. Sl. sol. boiling water.—BaA'_2 4aq.—CaA'_2 5aq: tufts of flattened needles.

CHLORO-METHACRYLIC ACID $C_4H_5ClO_2$. [59°]. From tri-chloro-isobutyric acid, HCl, and zinc-dust (Gottlieb, *J. pr.* [2] 12, 19). Formed also by heating an aqueous solution of sodium citra-di-chloro-pyrotartrate; or by passing chlorine into an aqueous solution of sodium citraconate (Swarts, *J.* 1873, 583; Morawski, *J. pr.* [2] 12, 369; *Sitz. W.* [2] 74, 39). Needles, volatile with steam.

Salts.—KA′ aq.—AgA′.—CaA'_2 3aq.—BaA'_2 4aq.—PbA'_2 aq.—CuA′(OH).

Ethyl ether EtA′. (157°).

Di-chloro-methacrylic acid $C_4H_4Cl_2O_2$. [64°]. (216°). Formed by the action of alkalis on tri-chloro-isobutyric acid (Gottlieb, *J. pr.* [2] 12, 8; Morawski, *C. C.* 1877, 131). Slender prisms; may be sublimed. Attacks the skin. Sodium amalgam forms isobutyric acid.—NaA′ aq.—KA′ ½aq.—AgA′.—CaA'_2 2aq.—PbA'_2 aq. [100°].—CuA'_2.

CHLORO-METHANE *v.* Methyl chloride.

Di-chloro-methane *v.* Methylene chloride.

Tri-chloro-methane *v.* Chloroform.

Tetra-chloro-methane *v.* Carbon-tetrachloride, vol. i. p. 688.

CHLORO-METHANE-TRICARBOXYLIC ETHER $CCl(CO_2Et)_3$ (210°) at 140 mm. Prepared by chlorination of methane-tricarboxylic ether. By saponification it yields oxy-methane-tricarboxylic acid (carboxytartronic acid) (Conrad, *B.* 14, 618).

TRI-CHLORO-METHANE SULPHINIC ACID $CCl_3.SO_2H$. From tri-chloro-methane sulpho-chloride and alcoholic KCN or H_2S (Löw, *Z.* 1869, 82, 614; Rathke, *A.* 161, 149). Unstable needles.—Salts.—KA′. Its solution gives with Br a characteristic pp. of $CCl_3.SO_2Br$. Boiling water converts it into $CHCl_2(SO_3K)$. HNO_3 gives

$CCl_3SO_2NO_2$, a solid, volatile with steam; reduced by Zn and HCl to methyl mercaptan.—NH_4A': from $CCl_3.SO_2Cl$ and conc. NH_3Aq (McGowan, *C. J.* 51, 666).

CHLORO-METHANE SULPHONIC ACID $CH_2Cl.SO_3H$. Formed by the action of zinc and dilute H_2SO_4 on trichloro-methane sulphonic acid (Kolbe, *A.* 54, 168). Acid syrup. Sodium amalgam converts it into methane sulphonic acid. KA′: needles, insol. alcohol.—AgA′ crystalline.

Chloro-methane-disulphonic acid $CHCl(SO_3H)_2$. A by-product formed in the preparation of chloro-sulpho-acetic acid from chloro-acetic acid and $ClSO_3H$ (Andreasch, *M.* 7, 172). Very hygroscopic needles. **Salts**: BaA'_2 4aq: long thin shining needles. It is reduced by sodium amalgam in HCl solution to the methane disulphonate.—AgA′: circular aggregates.

Di-chloro-methane sulphonic acid ×$CCl_2H.SO_3H$.

Formation.—From $CCl_3.SO_2Cl$ and SO_2 in alcoholic solution (McGowan, *J. pr.* [2] 30, 297; *cf.* Gerhardt, *Compt. chim.* 1845, 197).

Preparation.—1. By action of Zn upon CCl_3SO_3H. The zinc is removed by K_2CO_3, and the potassium salt crystallised from alcohol (Kolbe).—2. By heating chloroform with aqueous K_2SO_3 (Strecker, *A.* 148, 92).

Salt.—A′K: thin plates or long prisms.—AgA′.

Chloride $CCl_2H.SO_2Cl$. (c. 175°). S.G. 1·7. From PCl_5 and the acid. An oil. Is *not* converted into CCl_3SO_2Cl by chloride of iodine.

Amide $CCl_2H.SO_2NH_2$. Formed by the action of dry NH_3 on the preceding. Crystallised from a mixture of benzene and alcohol.

Tri-chloro-methane sulphonic acid $CCl_3.SO_3H$.

Preparation.—Its chloride is digested with aqueous baryta; the barium is then removed by H_2SO_4 (McGowan, *J. pr.* [2] 30, 284).

Properties.—Small deliquescent prisms. Not volatile. Very acid.

Reactions.—1. Does not attack spongy *silver*; dissolves *iron* forming a ferrous salt; dissolves *zinc* forming di-chloro-methane sulphonate of zinc.—2. PCl_5 reacts, but without forming trichloromethane sulphochloride. PCl_5 does not even attack potassium tri-chloro-methane sulphonate.—3. Boiling conc. HNO_3, aqueous CrO_3, and aqua regia have no action.

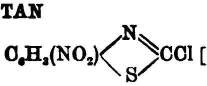
Salts.—KA′ aq.—FeA'_2 5aq.—PbA'_2 2aq.—AgA′aq.

Chloride. CCl_3SO_2Cl. [135°]. (170°). Formed by the action of chlorine and water on CS_2 (Berzelius a. Marcet, *Schw. J.* 9, 298). Prepared by exposing a mixture of CS_2, MnO_2, aqueous HCl and HNO_3 to sunlight (Kolbe, *A.* 54, 145). Crystallised from *dry* benzene. At 200° it splits up into SO_2, CCl_4, $COCl_2$, and $CSCl_2$ (Noelting, *Bl.* [2] 37, 392). *Reactions.*—1. Dissolves in conc. HNO_3, but is reppd. by water unaltered.—2. Boiling alcohol gives CCl_4 and SO_2 (Carius, *A.* 111, 105).—3. Aqueous or alcoholic KCN acts thus: $CCl_3.SO_2Cl + KCN = CNCl + CCl_3.SO_2K$ forming tri-chloro-methane sulphinate of potassium. A secondary reaction also occurs, thus: $CCl_3.SO_2K + KOH = KCl + CCl_2(OH)SO_2K$ (Loew, *Z.* 1868, 518; McGowan, *J. pr.* [2] 30, 288).—4. Reduced by H_2S or SO_2 in alcoholic solution to the sulphinic acid, $CCl_3.SO_2H$.—5. NH_3 forms tri-chloro-methane sulphinic acid and nitrogen in this way: $3CCl_3SO_2Cl + 8NH_3 = 3CCl_3.SO_2NH_4 + N_2 + 3NH_4Cl$. This reaction takes place whatever solvent is used.

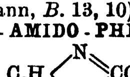
Anilide.—CCl_3SO_2NPhH. Needles. From aniline and the chloride, dissolved in alcohol or benzene, but not in ether.

Bromide.—$CCl_3.SO_2Br$. From tri-chloro methane sulphinic acid and Br (Loew, *Z.* 1869, 624). With alcohol at 100° it gives CCl_3Br and SO_2.

CHLORO - METHENYL - AMIDO - NITRO-PHENYL-MERCAPTAN

$C_7H_3O_2N_2ClS$ or 
$C_6H_3(NO_2)\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle CCl$ [1:2]

[192°]. Needles. Has no basic properties. Prepared by nitration of chloro-methenyl-amido-phenyl-sulphydrate (Hofmann, *B.* 13, 10).

CHLORO - METHENYL - AMIDO - PHENYL-MERCAPTAN C_7H_4ClNS or 
$C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle CCl$ [1:2]

[24°]. (248°). V.D. 82·4 (obs.). Prepared by heating phenyl-thio-carbimide with PCl_5 (Hofmann, *B.* 12, 1126; 13, 8). Crystalline solid. Weak base. The Cl atom is very readily replaced. It has none of the properties of a mustard oil and is incapable of uniting with amines to form thioureas.

CHLORO-METHYL-ACETO-ACETIC ETHER $C_7H_{11}ClO_3$. (180°). S.G. ^{15} 1·093. Formed, together with the di-chloro-ether, by treating methyl-aceto-acetic ether with PCl_5 (Isbert, *A.* 234, 188). With NaOEt (1 mol.) it gives $CH_2(OEt).CO.CHMe.CO_2Et$ (190°–195°). S.G. ^{22} ·976; whence alcoholic KOH gives $EtO.CH_2.CO.CH_2CH_3$.

Di-chloro-methyl-aceto-acetic ether $C_7H_{10}Cl_2O_3$. (210°–220°). S.G. ^{17} 1·225. Formed as above.

CHLORO-METHYL-AMIDO-BENZOIC ACID $C_6H_3Cl(NHMe)CO_2H$ [4:2:1] or [6:2:1]. [178°]. From the formyl derivative and alcoholic KOH. Fine white needles. V. sol. alcohol with a blue fluorescence, v. sl. sol. water.

Formyl derivative $C_6H_3Cl(NMe.COH)CO_2H$: [c. 202°]; fine white plates or needles; sl. sol. water, ether, and chloroform, v. sol. hot alcohol. Formed, together with chloro-methyl-isatin, by oxidation of the methylo-chloride of (*B.* 1 or 3)-chloro-quinoline with $KMnO_4$ (La Coste a. Bodewig, *B.* 18, 428).

***p*-CHLORO - TETRA - METHYL-*p*-DI-AMIDO-TRI-PHENYL-CARBINOL** $C_6H_4Cl.C(OH):(C_6H_4.NMe_2)_2$. [146°]. Colourless crystals. Easily soluble in benzene and ether. Formed by oxidation of the leuco-base the condensation-product of dimethylaniline and *p*-chlorobenzaldehyde. The zinc double chloride is a bluish-green dyestuff (Kaeswurm, *B.* 19, 744).

TRI-CHLORO-METHYL-*p*-AMIDO-PHENYL-ETHYL - ALCOHOL $Cl_3C.CH(OH)C_6H_4.NHMe$. [112°]. Formed by the action of chloral hydrate on methylaniline (Boessneck, *B.* 21, 782). Crystals (from alcohol).

Reactions.—1. *Sodium nitrite* added to a solution in HClAq forms a **nitroso- compound**

[118°]: needles, sol. alcohol, HOAc, and ether. 2. On heating with *alkalis* chloroform is split off, and methyl-amido-benzoic aldehyde is formed.

Salt.—B′HCl: thick prisms, v. sol. hot, v. sl. sol. cold, water.

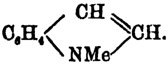
Tri-chloro-di-methyl-*p*-amido-phenyl ethyl alcohol $CCl_3.CH(OH).C_6H_4.NMe_2$. [111°]. White plates. Obtained by adding 5 pts. of powdered $ZnCl_2$ to a cooled mixture of 10 pts. of chloral hydrate and 40 pts. of dimethylaniline, and allowing the mixture to stand at about 50° for 24 hours; yield 7 pts. By boiling with aqueous or alcoholic KOH it is decomposed into chloroform and di-methyl-*p*-amido-benzaldehyde [73°].—B′HCl. Sparingly soluble colourless needles (Bœssneck, *B.* 18, 1516).

***p*-CHLORO-TETRA-METHYL-*p*-DI-AMIDO-TRI-PHENYL-METHANE** $C_6H_4Cl.CH(C_6H_4.NMe_2)_2$. [143°]. Obtained by heating together di-methyl-aniline and *p*-chloro-benzaldehyde in presence of $ZnCl_2$ (Kaeswurm, *B.* 19, 742). Small colourless concentric needles. Sol. benzene, alcohol and ether, sparingly in ligroïn, insol. water. On oxidation it gives the carbinol base which forms colourless crystals [146°], easily sol. benzene and ether, of which the zinc double chloride is a bluish-green dyestuff.

Salts.—$B''H_2Cl_2PtCl_4$: easily sol. yellow crystalline pp. The chloride and sulphate are easily soluble colourless salts.

Exo-**Di-chloro-di-methyl-di-amido-di-phenyl-methane** $CCl_2(C_6H_4NMe_2)_2$. From $CS(C_6H_4NMe_2)_2$ and BzCl in CS_2 (Baither, *B.* 20, 3289). Converted by water into the ketone $CO(C_6H_4NMe_2)_2$.

ω-CHLORO-METHYL-*o*-AMIDO-STYRENE $C_6H_4(NHMe).CH:CHCl$. Formed by methylation of chloro-amido-styrene (Lipp, *B.* 17, 2509). Liquid. V. sol. alcohol and ether, nearly insol. water. Volatile with steam. Heated with sodium ethylate at 130°–140° it is converted into methyl-indole



$C_6H_4\left\langle\begin{matrix}CH\\NMe\end{matrix}\right\rangle CH.$

ν-DI-CHLORO-METHYL-AMINE *v.* Methylamine.

CHLORO-METHYL-ANILINE C_7H_8ClN *i.e.* $C_6H_4Cl.NHMe$. (240°). Formed by treating $NMe(CHO).C_6H_3Cl.CO_2H$ with conc. HCl (La Coste a. Bodewig, *B.* 18, 430). Liquid.—B′HCl: [164°].

***m*-Chloro-methyl-aniline [3:1]** $C_6H_4Cl.NHMe$. *Acetyl derivative* $C_6H_4Cl.NMeAc$. [93°]. From *m*-chloro-di-methyl-aniline and AcBr (Staedel, *B.* 19, 1948). Tables, v. e. sol. benzene.

***p*-Chloro-methyl-aniline** *Nitrosamine.* $C_6H_4Cl.NMe.NO$. [51°]. From *p*-chloro-di-methyl-aniline and nitrous acid (Koch, *B.* 20, 2459).

***o*-Chloro-di-methyl-aniline** $C_6H_4Cl(NMe_2)$[1:2]. (206°). Formed by heating *o*-chloraniline hydrobromide (1 mol.) with methyl alcohol (rather more than 2 mols.) for 10 hours at 145°. Colourless fluid. The hydrochloride forms hygroscopic needles, the ferrocyanide white crystals, insol. water.—$B'_2H_2Cl_2PtCl_4$ (Heidlberg, *B.* 20, 149).

***m*-Chloro-di-methyl-aniline [3:1]** $C_6H_4Cl.NMe_2$. (232°). From *m*-chloro-aniline hydrobromide (a little over 2 mols.) and MeOH (1 mol.) by heating for 8 hours at 145° (Baur a. Staedel, *B.* 16, 32). AcBr decomposes it in the cold, displacing Me by Ac, and forming $C_6H_4ClNMeAc$ (Staedel, *B.* 19, 1948).—B′HBr: red plates.—B′HCl: slender needles.—$B'_2H_2PtCl_6$: slender yellow needles.

***p*-Chloro-di-methyl-aniline** $C_6H_4Cl.NMe_2$[1:4]. [36°]. (230°). Prepared by the action of Cu_2Cl_2 upon the diazo- compound of *u*-di-methyl-*p*-phenylene diamine. Large flat glistening needles. Sol. alcohol, ether, and benzene, insol. water. The ferrocyanide forms microscopic prisms.—$B'_2H_2Cl_2PtCl_4$: golden-yellow prisms (Heidlberg, *B.* 20, 151).

Di-chloro-di-methyl-aniline $C_6H_3Cl_2NMe_2$. (234°). From dimethylaniline and Cl or SO_2Cl_2 (Krell, *B.* 5, 878; Wenghöffer, *J. pr.* [2] 16, 462). Liquid.—$B'_2H_2PtCl_6$.

Tri-chloro-di-methyl-aniline $C_6H_2Cl_3NMe_2$. [32°]. (257°). From di-methyl-aniline and Cl (K.).—B′HCl.—$B'_2H_2PtCl_6$.

CHLORO-METHYL-BENZENE *v.* Chloro-toluene.

Chloro-di-methyl-benzene *v.* Chloro-xylene.

Chloro-tri-methyl-benzene *v.* Chloro-mesitylene and Chloro-ψ-cumene.

Chloro-tetra-methyl-benzene *v.* Chloro-durene.

Hexa-chlor-hexa-methyl-benzene $C_{12}H_{12}Cl_6$. [269°]. S.G. ^{15} 1·609. Probably $C_6(CH_2Cl)_6$. Formed by the action of PCl_5 upon $C_6(CH_3)_6$. Colourless, flattened prisms; commences to sublime at 269°; v. sl. sol. ether, or hot $CHCl_3$. In contact with boiling water, made slightly alkaline, it very slowly loses all its chlorine, giving a body of an alcoholic nature, [180°], v. sol. acids; which is sol. alcohol, sl. sol. ether, v. sl. sol. water (Colson, *Bl.* [2] 46, 197).

Hexa-chlor-hexa-methyl benzene $C_{12}H_{12}Cl_6$. [147°]. $C_6(CCl_3)(CH_2Cl)_3(CH_3)_2$. Formed together with the preceding symmetrical isomeride by the action of PCl_5 upon $C_6(CH_3)_6$. Colourless crystals; sol. $CHCl_3$. Boiling water, slightly alkaline, removes its chlorine. The product is an alcohol-acid, probably $C_6(CH_2OH)_3(CH_3)_2(CO_2H)$ (Colson, *Bl.* [2] 46, 198).

TRI-CHLORO-TRI-METHYL-CARBINYL CHLORIDE *v.* Tetra-chloro-isobutane.

TRI-CHLORO-DI-METHYL CARBONATE $CO(OMe)(OCCl_3)$. (91°) at 42 mm. Formed by acting on methyl alcohol with $ClCO_2CCl_3$ (Hentschel, *J. pr.* [2] 36, 314).

Hexa-chloro-di-methyl-carbonate $CO(OCCl_3)_2$. [79°]. Distils undecomposed. Colourless crystals. Prepared by the action of Cl on methyl carbonate (Councler, *B.* 13, 1698).

CHLORO-METHYL-*pseudo*-CARBO-STYRIL *v.* Chloro-oxy-methyl-quinoline.

β-CHLORO-α-METHYL CROTONIC ACID $CH_3.CCl:CMe.CO_2H$. [69·5°]. Solidifies at 65°. (210°). From methyl-aceto-acetic ether and PCl_5 (Isbert, *A.* 234, 188). Laminæ (from hot water).

Salts.—MgA'_2 2aq.—ZnA′ 1½aq.

Reactions.—1. NaOEt forms the ethyl derivative of β-oxy-α-methyl-crotonic acid.—2. Conc. KOHAq forms methyl ethyl ketone and CO_2: chloro-butylene is not formed as Demarçay asserts.

Ethyl ether EtA′. (173°).

PER-CHLORO-TRI-METHYL-CYANIDINE *v.* *Paranitrile of* Tri-chloro-acetic acid

CHLORO-TRIMETHYLENE GLYCOL *v.* Glycerin (β)-chlorhydrin.

CHLORO-METHYL ETHER *v.* Chloro-di-methyl oxide.

CHLORO-METHYL-ETHYL-GLYOXALINE $C_6H_9ClN_2$. *Chloro-oxal-ethyline.* (218°). S.G. ^{15} 1·142. From either di-ethyl-oxamide by PCl_5 (Wallach, *A.* 184, 37; 214, 261). Symmetrical di-ethyl-oxamide gives a good yield, the unsymmetrical a bad yield. CONEtH.CONEtH gives, doubtless, NEt:CCl.CCl:NEt as intermediate product. $CONEt_2.CONH_2$ should give $CCl_2NEt_2.CN$ as intermediate product, but this then changes to CClNEt.CClNEt by intra-molecular change. This view is supported by the production of chloro-oxal-ethyline by the action of PCl_5 on di-ethyl-oxamo-nitrile, $NEt_2.CO.CN$.

Properties.—Liquid, with narcotic odour, v. e. sol. alcohol, ether, ligroin, and $CHCl_3$. Changed by frequent distillation into an isomeric modification (220°–224°), insol. ligroin. Water at 290° decomposes it, giving NH_3 and NH_2Et.

Reactions.—1. Br in CS_2 or $CHCl_3$ forms B'HBr, $C_6H_8BrClN_2Br_2HBr$ [113°], forming red needles, and $C_6H_8BrClN_2Br_2$ [133°]. Both bodies are unstable, and give, when boiled with water, chloro-bromo-oxal-ethyline.—2. $KMnO_4$ gives oxalic acid.—3. Dilute H_2SO_4 at 240° forms NH_3 and $NEtH_2$.—4. Conc. H_2SO_4 at 220° gives acetic acid.—5. Distilled over *lime* it forms para-oxal-methyline.—6. Na added to its solution in light petroleum forms di-oxal-ethyline, $C_{12}H_{18}N_4$.—7. P and HI at 170° reduces it to oxal-ethyline.

Salts.—$B'_2H_2PtCl_4$.—B'HI aq.—$B'H_2ZnCl_4$. B'HBr. B'HCl aq.—$B'HgCl_2$.—$B'4HgCl_2$.—$B'I_2$ [110°].—$B'AgNO_3$.—$B'H_2C_2O_4$.

Methylo-iodide B'MeI: [205°]; needles (from alcohol).

CHLORO-METHYL-TRI-ETHYL-PHOSPHONIUM CHLORIDE $CH_2Cl.PEt_3Cl$. From methylene chloride and PEt_3 (Hofmann, *Pr.* 11, 290); $CH_2(PEt_3Cl)_2$ being formed at the same time. Formed also by the action of water on the compound of PEt_3 and CCl_4.—$(CH_2Cl.PEt_3Cl)_2PtCl_4$. Slightly soluble needles.

CHLORO-METHYL-GLYOXALINE $C_4H_5ClN_2$. *Chloro-oxalmethyline.* (205°). V.D. 4·1 (obs.). S.G. ^{16} 1·247.

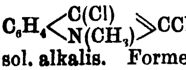
Preparation.—Pure di-methyl-oxamide (10 pts.) is mixed with PCl_5 (33 pts.) in the cold. On warming HCl is evolved. The product is distilled under diminished pressure, and afterwards with steam, and is finally extracted by shaking with $CHCl_3$ (Wallach, *B.* 14, 422; *A.* 214, 308).

Properties.—Liquid; reduced by HI to methyl-glyoxaline.

Salts.—B'HI: needles, sol. water and alcohol.—$B'_2H_2PtCl_6$.

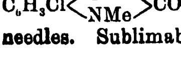
CHLORO-METHYL-GLYOXIM *v.* Chloro-iso-nitroso-acetone oxim.

DI-CHLORO-METHYL-INDOLE



$C_6H_4{<}\genfrac{}{}{0pt}{}{C(Cl)}{N(CH_3)}{>}CCl$. [59°]. Long needles. Insol. alkalis. Formed by methylation of chloro-oxindole-chloride (Baeyer, *B.* 15, 786).

CHLORO-METHYL-(PSEUDO)-ISATIN



$C_6H_3Cl{<}\genfrac{}{}{0pt}{}{CO}{NMe}{>}CO$. [191°]. Long fine red needles. Sublimable. Formed, together with the formyl derivative of chloro-methyl-amido-benzoic acid, by oxidation of the methylo-chloride of (*B.* 1or3)-chloro-quinoline with $KMnO_4$ (La Coste a. Bodewig, *B.* 18, 429).

TETRA-CHLORO-DI-METHYL-DI-KETONE (?) $CHCl_2.CO.CO.CHCl_2$. [84°]. (202°). A product of the action of $KClO_3$ and HCl on chloranilic acid (Levy a. Jedlicka, *B.* 21, 318). Large yellow tables (from ether). Pungent; sol. water. Forms a phenyl-hydrazide [186°].

PER-CHLORO-METHYL-MERCAPTAN CCl_3SCl (?). *Tri-chloro-methyl-sulphur chloride. Thiocarbonyl tetrachloride.* (149° uncor.). S.G. 1·722 at 0°; 1·7049 at 11°; 1·6953 at 17½°.

Formation.—1. From methyl sulphocyanide and dry chlorine; the yield is 83 p.c. of the sulphocyanide (James, *C. J.* 51, 272).—2. From CS_2 and chlorine (Rathke, *A.* 167, 180).—3. From $CSCl_2$ and Cl_2.

Preparation.—By passing chlorine (5 mols.) into cooled dry CS_2 (1 mol.) containing a trace of iodine; the product is freed from chloride of sulphur by treatment with water and distillation with steam, and is then fractionated *in vacuo*.

Properties.—Yellow oil, of very unpleasant strong smell. By long heating to its boiling-point it slowly decomposes, probably into CCl_4 and S.

Reactions.—1. By treatment with *chlorine* in presence of iodine it yields CCl_4 and S_2Cl_2.—2. *Alcohol* forms an oil, possibly CS_4Cl_3, and crystals of $C_3H_6O_2$ (126°).—3. *Water* at 160° splits it up into CO_2, HCl, and S. *Alkalis* act in the same way.—4. By heating with *sulphur* at 150°–160° it yields CS_2, CCl_4, $CSCl_2$, per-chloro-methyl tri-sulphide $(CCl_3)_2S_3$ and per-chloro-methyl di-sulphide $(CCl_3)_2S_2$; but the latter appears to be the primary product: $2CCl_3.SCl + S_2 = (CCl_3)_2S_2 + S_2Cl_2$. Per-chloro-methyl-di-sulphide is also formed by heating per-chloro-methyl mercaptan with silver-powder, thus: $2CCl_3.SCl + Ag_2 = (CCl_3)_2S_2 + 2AgCl$ (Klason, *B.* 20, 2376).—5. By $SnCl_2$ it is reduced to $CSCl_2$.—6. HNO_3 (S.G. 1·2) oxidises it to $CCl_3.SO.Cl$.—7. K_2SO_3 gives $C(SH)(SO_3K)_3$.—8. *Aniline* (2 mols.) forms $CCl_3.S.NHPh$; an unstable oil converted by excess of aniline into di-amid-di-phenyl sulphide, di-phenyl-thio-urea, and tri-phenyl-guanidine; and converted by alcoholic KOH into $CCl_2.S.NPh$ (?) [140°] (Rathke, *A.* 167, 211; *B.* 19, 395).—9. The analogous compound $CCl_3.S.NHC_6H_4(CH_3)$ is formed by adding (2 mols. of) *p*-toluidine to its ethereal solution. This body is crystalline, and by boiling with alcohol it is decomposed into *p*-toluidine, CO_2 and H_2S; alcoholic KOH splits off HCl, giving a body [138°], which probably has the constitution $CCl_2.S.N.C_6H_4Me$ (Rathke, *B.* 19, 395).

HEXA-CHLORO-METHYL-METHYLENE DI-KETONE $(CCl_3.CO)_2.CH_2$; (258°). (c. 192°) at 20 mm. Is the final substitution product obtained by the prolonged action of chlorine upon acetyl-acetone at 120°–130°, and in direct sunlight. Colourless liquid, decomposes when distilled under ordinary pressure. Treated with NaOH (1 mol.) it gives tri-chlor-acetone and sodium tri-chlor-acetate (Combes, *A. Ch.* [6] 12, 238).

ω-CHLORO-(β)-METHYL-NAPHTHALENE $C_{10}H_7.CH_2Cl$. [47°]. (168° at 20 mm.). White glistening plates. Formed by passing chlorine into (β)-methyl-naphthalene heated to about 250° (Schulze, *B.* 17, 1529).

CHLORO-DI-METHYL OXIDE C_2H_5ClO *i.e.* $CH_2Cl.O.CH_3$. (60°). From di-methyl oxide and Cl in daylight (Friedel, *Bl.* [2] 24, 161; 28, 171; *C. R.* 84, 247; Kleber, *A.* 246, 97). Decomposed by water into HCl, MeOH, and formic paraldehyde (trioxymethylene). Ammonia forms hexa-methyleneamine. KOAc gives $CH_3.O.CH_2.OAc$ (118°); which is decomposed by water.

Di-chloro-di-methyl oxide $(CH_2Cl)_2O$. (105°). V.D. 3·9 (calc. 4·0). S.G. ^{20} 1·318. From Me_2O and Cl in daylight (Regnault, *A.* 34, 31; *A. Ch.* [2] 71, 396). Decomposed by boiling water into HCl, formic acid, and formic paraldehyde (Butlerow, *Z.* 1865, 618).

Tetra-chloro-di-methyl oxide $(CHCl_2)_2O$. (130°). V.D. 6·4 (calc. 6·5). S.G. ^{20} 1·606. From Me_2O and Cl (Regnault, *A. Ch.* [2] 71, 396).

Hexa-chloro-di-methyl oxide $(CCl_3)_2O$. (100°). S.G. 1·597. From Me_2O and Cl in sunshine (Regnault). Decomposed on vaporisation, the V.D. being only 4·67.

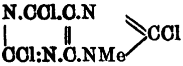
Tri-**CHLORO-METHYL-PARACONIC ACID** *v.* TRI-CHLORO-OXY-ETHYL-SUCCINIC ACID.

DI-CHLORO-DI-METHYL-*p*-PHENYLENE-DIAMINE $C_6H_2Cl_2(NMe_2)(NH_2)$ [5:2:4:1]. Formed, together with di-methyl-*p*-phenylene diamine and di-chloro-*p*-phenylene-diamine by boiling nitroso-di-methyl-aniline with HCl (1·2 S.G.). By $K_2Cr_2O_7$ and H_2SO_4 it is oxidised to di-chloro-quinone [159°]. By treatment with Fe_2Cl_6 in presence of H_2S and $ZnCl_2$ it yields di-chloro-methylene blue (Möhlau, *B.* 19, 2010).

CHLORO-METHYL ISOPROPYL KETONE C_5H_9ClO *i.e.* $CH_2Cl.CO.Pr$. (c. 120°). From petroleum pentane (?) or inactive amyl chloride by treatment with CrO_2Cl_2 followed by water (Etard, *C. R.* 84, 127). Insol. water and aqueous KOH; reduces ammoniacal $AgNO_3$. Does not combine with $NaHSO_3$.

TRI-CHLORO-METHYL-PURIN

$C_5(CH_3)Cl_3N_4$ *i.e.*



$$\begin{array}{l}\mathrm{N.CCl.C.N}\\ |\qquad\quad\ \|\qquad\quad \rangle\mathrm{CCl}\\ \mathrm{CCl{:}N.C.NMe}\end{array}$$

(?) [174°].

Small colourless crystals. Insol. alkalis. Formed by heating di-chloro-oxy-methyl-purin with PCl_5 and $POCl_3$ at 160° for eight hours. Heated with alcoholic NaOH it yields chloro-di-ethoxy-methyl-purin, which by HCl at 130° is converted into methyl-uric acid (Fischer, *B.* 17, 331, 1787).

CHLORO-α-METHYL-PYRIDINE C_6H_6ClN. *Chloro-(α)-picoline.* [21°]. (165° uncor.). S.G. ^{20} 1·146. Formed by reducing the mixture of penta- and hexa-chloro- picolines obtained by heating comenamic acid with PCl_5. The mixture is heated at 210° with a solution of HI in glacial acetic acid (Ost, *J. pr.* [2] 27, 278).

Properties.—Colourless prisms. Smells like pyridine. Nearly insoluble in water, insoluble in potash, soluble in alcohol and in ether.

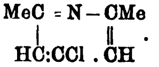
Salts.—B′,HCl. Prisms.- $\{B',HCl\}_2PtCl_4$. Needles or prisms.

Chloro-methyl-pyridine C_6H_6ClN. (160°–170°). From potassium methyl-pyrrol and $CHCl_3$ (Ciamician a. Dennstedt, *B.* 14, 1162).—$B'_2H_2PtCl_6$.

Hexa-chloro-methyl-pyridine $C_5HCl_3N(CCl_3)$. [60°]. The chief product of the action of PCl_5 (7 mols.) on comenamic (di-oxy-pyridine carboxylic) acid at 290° (Ost, *J. pr.* [2] 27, 277). May be distilled with steam.

Properties.—Large oblique prisms, or plates (from alcohol). Insol. water, acids and bases.

Chloro-di-methyl-pyridine



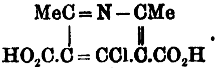
$$\begin{array}{l}\mathrm{MeC=N-CMe}\\ \quad|\qquad\quad \|\\ \mathrm{HC{:}CCl\,.\,CH}\end{array}$$

. *Chloro-lutidine.* (178°). S.G. 1·105 at 17°. Formed by heating oxy-di-methyl pyridine (leitidone) with PCl_5 at 140°; the yield is 50 p.c. Colourless oil. Sl. sol. water.

Salts.—The hydrochloride forms slender needles.—$B'_2H_2Cl_2PtCl_4$: orange crystalline pp. —$^{x}B'_2H_2Cl_2HgCl_2$: [155°], sl. sol. water. Chloro-di-methyl-pyridine suspended in water gives characteristic pps. with picric acid $K_2Cr_2O_7$, $CuSO_4$, and $AgNO_3$ (Conrad a. Epstein, *B.* 20, 164).

Tri-chloro-di-methyl-pyridine $C_7H_6Cl_3N$. Formed by chlorinating (β)-lutidine in presence of iodine (Greville Williams, *C. N.* 44, 308).—$B'_2H_2PtCl_6$.

CHLORO-DIMETHYL-PYRIDINE CARBOXYLIC ACID

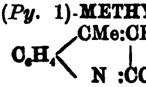


$$\begin{array}{l}\quad\ \mathrm{MeC=N-CMe}\\ \qquad\ |\qquad\quad \|\\ \mathrm{HO_2C.C=CCl.C.CO_2H}\end{array}$$

. *Chloro-lutidine-di-carboxylic acid.* [c. 224°]. Formed by the action of PCl_5 upon oxy-di-methyl-pyridine-di-carboxylic acid (lutidone-di-carboxylic acid) at 140°. White prisms. Sol. hot water (Conrad a. Epstein, *B.* 20, 164).

Penta-chloro-tri-methyl-pyridine di-carboxylic ether. *Di-chloride.* [150°]. From hydro-tri-methyl-pyridine di-carboxylic ether by chlorination (Hantzsch, *A.* 215, 19). Woolly needles (from alcohol).

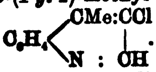
(*Py.* 3)-**CHLORO**-(*Py.* 1)-**METHYL-QUINOLINE** $C_{10}H_8NCl$ *i.e.*



$$\mathrm{C_6H_4}\Big\langle\begin{array}{l}\mathrm{CMe{:}CH}\\ \qquad\quad |\\ \mathrm{N\ \ {:}CCl}\end{array}$$

. [59°]. (296° cor.). From (*Py.* 3)-oxy-(*Py.* 1)-methyl-quinoline and PCl_5 (Knorr, *A.* 236, 97). Mass of slender needles (from dilute alcohol); v. sl. sol. water, v. sol. alcohol and ether; volatile with steam.—$B'_2H_2PtCl_6$ 2aq. Reduced by HI to (*Py.* 1)-methyl-quinoline. Water at 160° has no action: at 200° it converts it into oxy-methyl-quinoline.

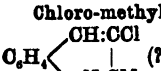
(*Py.* 2)-**Chloro**-(*Py.* 1)-**methyl-quinoline** C_9H_5MeClN *i.e.*



$$\mathrm{C_6H_4}\Big\langle\begin{array}{l}\mathrm{CMe{:}CCl}\\ \qquad\ |\\ \mathrm{N\ :\ CH}\end{array}$$

. [54°]. From skatole, chloroform, and alcoholic NaOH (Magnanimi, *G.* 17, 252). Delicate needles. Its picric acid compound melts at 208°, and its aurochloride at 164°.

Chloro-methyl-quinoline C_9H_5MeClN *i.e.*

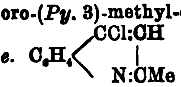


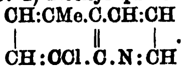
$$\mathrm{C_6H_4}\Big\langle\begin{array}{l}\mathrm{CH{:}CCl}\\ \quad\ |\\ \mathrm{N{:}CMe}\end{array}$$

(?). [71°]. From methyl-ketole, chloroform, and alcoholic NaOH, thus:

$$\begin{aligned}&C_8H_6MeN + 2NaOH + CHCl_3\\ &= C_9H_5MeClN + 2NaCl + 2H_2O\end{aligned}$$

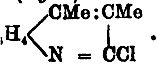
(Magnanimi, *G.* 17, 249). White needles, insol. water, sol. alcohol and ether. The picric acid compound forms pale yellow needles [223°].

(*Py* 1)-Chloro-(*Py.* 3)-methyl-quinoline C_9H_5MeClN *i.e.*  . (γ)-*Chloroquinaldine.* [43°]. (270°). From PCl_5 and oxy-methyl-quinoline, the product of condensation of aceto-acetic ether with aniline (Conrad a. Limpach, *B.* 20, 944). Water at 220° gives oxy-methyl-quinoline. HI in HOAc at 260° gives methyl-quinoline. The picric acid compound melts at 178°.—$B'_2H_2PtCl_6$.—B'HBr.

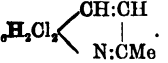
(*B.* 4)-Chloro-(*B.* 1)-methyl-quinoline C_9H_5MeClN *i.e.* 

$$\begin{array}{c}CH{:}CMe.C.CH{:}CH\\ |\qquad\quad \|\qquad |\\ CH{:}CCl.C.N{:}CH\end{array}$$

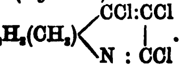
. [49°]. From (6, 3, 1)-chloro-*m*-toluidine, nitro-benzene, glycerin, and H_2SO_4 (Gattermann a. Kaiser, *B.* 18, 2603). Needles; v. sol. alcohol, ether, and benzene. HI in HOAc converts it at 250° into (*B.* 1)-methyl-quinoline. The picric acid compound melts at 172°.—$B'HCl.HgCl_2$.—$B'_2H_2IrCl_6$.

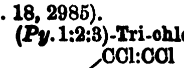
(*Py.* 3)-Chloro-(*Py.* 2,3)-di-methyl-quinoline  . [131°]. From oxy-di-methyl-quinoline and PCl_5 (Knorr, *A.* 245, 360). Crystals (from alcohol). Water at 200° forms again the di-methyl-carbostyril.—$B'_2H_2PtCl_6$ 4aq.

(*Py.* 1)-Chloro-(*Py.* 3; *B.* 2·4)-tri-methyl-quinoline $C_9H_3NClMe_3$. *o-p-Di-methyl-γ-chloro-quinaldine.* [114°]. (298°). Formed by the action of PCl_5 in presence of $POCl_3$ on (*Py.* 1:3; *B.* 2:4)-Oxy-tri-methyl-quinoline (Conrad a. Limpach, *B.* 21, 527). Flat prisms (from ether). Sublimes easily. Almost insol. water, v. sol. dilute acids, alcohol, ether, and benzene. On heating with aniline the chlorine is replaced by NHPh.—$(B'HCl)_2PtCl_4$: Needles; v. sl. sol. hot water.

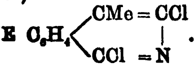
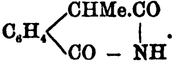
Di-chloro-(*Py.* 3)-methyl-quinoline  . *Di-chloro-quinaldine.* [46°]. (300°). Obtained by heating di-chloro-*o*-amido-benzaldehyde with sodium acetate and aqueous NaOH (Gnehm, *B.* 17, 755).

Di-chloro-(*B.* 1)-methyl-quinoline $C_9H_4NMeCl_2$. [275°]. Formed by dissolving (*B.* 1)-methyl-quinoline in boric acid and treating this with a solution of bleaching powder (Einhorn a. Lauch, *A.* 243, 361). Needles (from acetic ether).

(*Py.* 1:2:3)-Tri-chloro-(*B.* 4)-methyl-quinoline  . *Tri-chloro-toluquinoline.* [112°]. Formed by heating (*Py.* 2:3:1)-di-chloro-oxy-(*B.* 4)-methyl-quinoline with PCl_5 at 125°. Long colourless needles. Very volatile with steam. Peculiar smell (Rügheimer a. Hoffmann, *B.* 18, 2985).

(*Py.* 1:2:3)-Tri-chloro-(*B.* 2)-methyl-quinoline  . *Tri-chloro-toluquinoline.* [134°]. *Formation.*—1. By the action of PCl_5 upon malon-phenyl-amic acid.—2. The acid malonate of *p*-toluidine (5 g.) is covered with benzene (50 g.) and PCl_5 (25 g.) slowly added; after standing for some time the reaction is completed by heating to boiling.

Properties.—Long colourless needles. Sol. alcohol, ether, benzene, &c., insol. water. Volatile with steam. Peculiar smell. Weak base (Rügheimer a. Hoffmann, *B.* 17, 740; 18, 2975, 2979).

(*Py.* 2:4:1)-DI-CHLORO-METHYL-ISO-QUINOLINE  . [102°]. Formed by the action of $POCl_3$ upon the imide of phenyl-methyl-acetic-*o*-carboxylic acid  . Long flat needles (Gabriel, *B.* 20, 2504).

DI-CHLORO-DI-METHYL-SUCCINIC ACID $C_6H_8Cl_2O_4$ *i.e.* $CO_2H.CClMe.CClMe.CO_2H$. *Di-chloro-adipic acid.* [185°]. Formed, together with pyrocinchonic acid, by the action of 'molecular' silver upon α-di-chloro-propionic acid in benzene solution (Otto a. Beckurts, *B.* 18, 847). Small crystals. Sublimable. V. sol. water and alcohol, v. sl. sol. benzene.

Reactions.—By further action of 'molecular' silver it is converted into pyrocinchonic acid $CO_2H.CMe{:}CMe.CO_2H$. On reduction it gives as chief product di-methyl-succinic acid $CO_2H.CHMe.CHMe.CO_2H$ [194°]. By the action of alcoholic KOH, or by heating the silver salt with water, chlorotiglic acid $C_4H_6Cl(CO_2H)$ is formed of melting-point [69°].

Salts.—$A''Na_2$: plates.—$A''K_2$ 2aq: plates.—$A''Ag_2$: white crystalline pp.

PER-CHLORO-METHYL-DI-SULPHIDE $(CCl_3)_2S_2$. (135° *in vacuo*). Obtained by the action of silver-powder upon per-chloro-methyl-mercaptan: $2\,CCl_3.SCl + Ag_2 = (CCl_3)_2S_2 + 2\,AgCl$. Also formed by heating per-chloro-methyl-mercaptan with sulphur. Thick yellowish oil, of slight turpentine-like smell. By distillation at the ordinary pressure it decomposes into $CCl_3.SCl$, $CSCl_2$, and other products. By heating with sulphur at about 170° it yields per-chloro-methyl tri-sulphide $(CCl_3)_2S_3$ (Klason, *B.* 20, 2379).

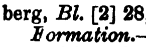
Per-chloro-methyl-tri-sulphide $(CCl_3)_2S_3$. [57°]. (190° *in vacuo*). Formed by heating per-chloro-methyl di-sulphide with sulphur at 170° (Klason, *B.* 20, 2380); or by passing chlorine into CS_2 containing iodine (Rathke, *A.* 167, 209). Flat prisms; v. e. sol. ether, CS_2, and warm alcohol. On distillation at the ordinary temperature it decomposes into $CCl_3.SCl$, $CSCl_2$, S, and other products.

TRI-CHLORO-METHYL-SULPHUR-CHLORIDE *v.* PER-CHLORO-METHYL-MERCAPTAN.

CHLORO-METHYL-UREA.

Acetyl derivative $C_4H_6Cl_2N_2O_2$ *i.e.* $CH_2Cl.NH.CO.NH.CO.CH_2Cl$. [180°]. From chloro-acetamide, Br, and aqueous KOH (Hofmann, *B.* 18, 2735). Decomposed by acids and alkalis into formic aldehyde and chloro-acetic acid.

CHLORO-MUCONIC ACID *v.* MUCONIC ACID.

(*d*)-CHLORO-NAPHTHALENE $C_{10}H_7Cl$ *i.e.*  . (251°) (F. a. S.); (263°) (Atterberg, *Bl.* [2] 28, 509). S.G. $\frac{0}{4}$ 1·20 (C.).

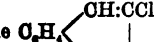
Formation.—1. By heating (α)-diazonaphthalene with a large excess of HCl; the yield is

38 p.c. of the theoretical (Gasiorowski a. Waÿss, *B.* 18, 1939).—2. By boiling naphthalene dichloride $C_{10}H_8Cl_2$ with alcoholic KOH (Laurent, *A.* 8, 13; Faust a. Saame, *A.* 160, 68; *Z.* [2] 5, 705).—3. By the action of PCl_5 on (α)-nitro-naphthalene (De Koninck a. Marquart, *B.* 5, 11) or on naphthalene (α)-sulphonic acid (Carius, *A.* 114, 145). 4. From (α)-nitro-naphthalene and Cl (Atterberg, *B.* 9, 317, 927).

Preparation.—By chlorinating naphthalene, washing with alcoholic potash and fractionating (Roux, *Bl.* [2] 45, 515).

Properties.—Liquid, not solid at −17°. In CS_2 solution it is not much acted upon by Al_2Cl_6, but if (α)-chloro-naphthalene is warmed with 20 p.c. of its weight of Al_2Cl_6, some naphthalene and tarry matters are produced together with the (β)- compound. In this reaction, therefore, it behaves in a similar manner to (α)-bromo-naphthalene. **Picric acid compound** [137°].

(β)-Chloro-naphthalene



$C_6H_4\left\langle\begin{matrix}CH{:}CCl\\ |\\ CH{:}CH\end{matrix}\right.$ [57°].

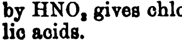
(252°); (265° cor.). S.G. ^{16} 1·266 (R.).

Formation.—1. By heating (β)-diazonaphthalene with a large excess of HCl; the yield is 45 p.c. of the theoretical (Gasiorowski a. Waÿss, *B.* 18, 1940; *cf.* Liebermann a. Palm, *A.* 183, 270). -2. By the action of PCl_5 on (β)-naphthol or on naphthalene (β)-sulphonic acid (Rimarenko, *B.* 9, 663; Clève, *Bl.* [2] 25, 257).—3. From $Hg(C_{10}H_7)_2$ and $SOCl_2$ (Heumann a. Köchlin, *B.* 16, 1627).—4. By intra-molecular change from (α)-chloro-naphthalene (*q. v.*).

(1:2)-Di-chloro-naphthalene $C_{10}H_6Cl_2$ [1:2] [35°]. Formed by dropping a solution of potassium nitrite (4 g.) in water (20 c.c.) into a boiling solution of (α)-chloro-(β)-naphthylamine hydrochloride (10 g.) and cuprous chloride (5 g.) in hydrochloric acid; yield—4 g. Also from (α)-chloro-(β)-naphthol and PCl_5 and from chloro-(α)-naphthylamine (obtained by reduction of di-chloro-α-naphthylamine) by replacing NH_2 by Cl. Monosymmetric tables, $a{:}b{:}c = 1{\cdot}5196{:}1{:}?$, $\beta = 76° 46'$ (Clève, *B.* 20, 1991). On nitration it yields di-chloro-di-nitro-naphthalene [170°]. CrO_3 forms di-chloro-naphthoquinone [181°].

(η)- or **(1,3′)-Di-chloro-naphthalene** $C_{10}H_6Cl_2$. [48°]. From naphthalene (β)-sulphonic acid by nitration and treatment of the resulting (β)-nitro-naphthalene (β-)-sulphonic acid with PCl_5 (Clève, *Bl.* [2] 29, 499). Also from (β)-naphthylamine (γ)-sulphonic acid by exchanging NH_2 for Cl and treating the product with PCl_5 (Forsling, *B.* 20, 2105). Also from ('β')-naphthalene-di-sulphonic acid and PCl_5 (Armstrong a. Wynne); and synthetically from *m*-chloro-phenyl-isocrotonic acid (Erdmann a. Kirchhoff). Oxidation by HNO_3 gives chloro-phthalic and nitro-phthalic acids.

(θ) or **(1:3)-Di-chloro-naphthalene**



$C_6H_4\left\langle\begin{matrix}CCl{:}CH\\ CH{:}CCl\end{matrix}\right\rangle$. [61° uncor.]. (286° uncor.).

Formation.—1. From (δ)-nitro-naphthalene (β)-sulphonic acid and PCl_5 (Clève, *Bl.* [2] 29, 415). — 2. From di-chloro-(α)-naphthylamine [82°] by the diazo- reaction.

Properties.—Flat glistening plates, or slender white needles; may be sublimed. By HNO_3 it is oxidised to phthalic acid (Clève, *B.* 20, 449). The so-called 'α'-di-chloro-naphthalene [38°] is a mixture of the θ and 'β'- isomerides. It gives a sulphochloride [148°].

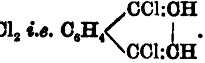
Di-chloro-naphthalene $C_{10}H_6Cl_2$ [1:2′]. [64°].

Formation.—1. From β-chloro-naphthalene sulphonic acid and PCl_5 (Arnell, *Bl.* [2] 45, 184; Armstrong a. Wynne, *C. J. Proc.* 4, 106). - 2. From (β)-naphthol-('α')-sulphonic acid (Bayer's acid) by heating with PCl_5 (Claus a. Volz, *B.* 18, 3157).—3. From (β)-naphthylamine-('α')-sulphonic acid (Badische acid) (Forsling).—4. From chloro-β-naphthol [101°] and PCl_5 (C. a. V.). - 5. From *p*-chloro-phenyl-paraconic acid (Erdmann a. Kirchhoff, *A.* 247, 379).

It gives a sulphochloride [119°].

('β') or (1,4)-Di-chloro-naphthalene

$C_{10}H_6Cl_2$ *i.e.*

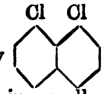


$C_6H_4\left\langle\begin{matrix}CCl{:}CH\\ |\\ CCl{:}CH\end{matrix}\right.$. [68°]. (287°).

Formation.—1. By distillation of naphthalene tetrachloride (Krafft a. Becker, *B.* 9, 1089; Faust a. Saame, *A.* 160, 70). -2. From naphthalene and Cl_2O (Hermann, *A.* 151, 63).—3. From (α)-chloro-naphthalene in $CHCl_3$ and Cl (Widmann, *Bn.* II, 139).—4. By the action of PCl_5 on (α)-nitro-(α)-naphthol (Atterberg, *B.* 9, 1189), on bromo-naphthalene sulphonic acid (Jolin, *Bl.* [2] 28, 516), or on chloro-naphthalene sulphonic acid, obtained from (α)-naphthylamine-*p*-sulphonic acid (Cleve, *Bl.* [2] 26, 242).

Properties.—Needles (from alcohol). Boiling dilute HNO_3 forms di-chloro-phthalic acid. CrO_3 in HOAc gives di-chloro-naphthoquinone [174°].

(ζ) or *Peri*-Di-chloro-naphthalene $C_{10}H_6Cl_2$, probably



(Ekstrand, *B.* 18, 2881). [83°]. Formed in small quantity on distilling 'β'-di-nitro-naphthalene with PCl_5 (Atterberg, *B.* 9, 1732). Formed also by nitrating (γ)-di-chloro-naphthalene, reducing this to chloro-naphthylamine [91°] and displacing NH_2 by Cl (Atterberg, *B.* 10, 548). Prisms.

(κ)-Di-chloro-naphthalene $C_{10}H_6Cl_2$. [94° uncor.]. Formed by heating (α)-naphthol sulphonic acid with PCl_5 (Claus a. Oeler, *B.* 15, 314). On moderate oxidation it gives (α)-naphthoquinone and by further oxidation phthalic acid.

(γ)-Di-chloro-naphthalene $C_{10}H_6Cl_2$ [1:4′]? (Ekstrand, *B.* 18, 2881). [107°]. Formed by the action of PCl_5 on (α)-nitro-naphthalene, or, better, on ('α')-di-nitro-naphthalene (Atterberg, *B.* 9, 317, 1188, 1734), and on (α)-nitro-naphthalene (α)-sulphonic acid (Cleve, *Bl.* [2] 24, 506). Also from (α)-naphthylamine sulphonic acid (Laurent's naphthalidinic acid) by diazotisation and distillation of the resulting diazo-naphthalene sulphonic acid with PCl_5 (Erdmann, *B.* 20, 3185). Formed synthetically from *o*-chloro-phenyl-paraconic acid. Scales. Gives a nitro-derivative [142°], and a di-nitro-derivative [246°]. Oxidation by HNO_3 gives chloro-nitro-phthalic acid. CrO_3 in HOAc gives *c*-chloro-phthalic acid [184°] (Guareschi, *G.* 17, 119).

(δ)-Di-chloro-naphthalene $C_{10}H_6Cl_2$. [114°]. From naphthalene-('α')-di-sulphonic acid and PCl_5 (Clève, *Bl.* [2] 26, 244). Large tables; v. sol. boiling alcohol. Dilute HNO_3 gives chloro-phthalic acid. It is perhaps $C_{10}H_6Cl_2$ [2:2′].

(ι)-Di-chloro-naphthalene $C_{10}H_6Cl_2$. [120°]. From naphthalene tetrachloride (4 pts.) and

Ag_2O (3 pts.) at 200° (Leeds a. Everhart, *Am.* 2, 211). Formed, in very small quantity, when $C_{10}H_8Cl_4$ is decomposed by alcoholic KOH (Widmann, *B.* 15, 2162). Very thin laminæ; sl. sol. cold alcohol.

(ε) or (2, 3')?-Di-chloro-naphthalene $C_{10}H_6Cl_2$. [136°]. (285° uncor.).

Formation.—1. By distilling (β)-chloro-naphthalene-sulphonic chloride with PCl_5; the chloro-naphthalene-sulphonic acid being obtained either by sulphonation of (β)-chloro-naphthalene or by the action of cuprous chloride upon the diazo-compound from the (β)-naphthylamine sulphonic acid obtained from (β)-naphthol sulphonic acid and NH_3 (Forsling, *B.* 20, 81; Arnell, *Bl.* [2] 45, 184).—2. From naphthalene ('β')-disulphonic acid, and from (β)-naphthol (α)-sulphonic acid by distilling with PCl_5 (Clève, *Bl.* [2] 25, 244; Armstrong a. Graham, *C. J.* 39, 142; Claus a. Zimmermann, *B.* 14, 1483). Needles (by sublimation) or large monoclinic tables (from alcohol). Volatile with steam. Sol. ether, chloroform, and benzene, sl. sol. alcohol. On oxidation it gives chloro-phthalic acid $C_6H_3Cl(CO_2H)_2$ [4:2:1] and ('β')-di-chloro-(α)-naphthoquinone [149°] (Claus a. Muller, *B.* 18, 3073).

(ζ)-Tri-chloro-naphthalene $C_{10}H_5Cl_3$. [56°]. Prepared by heating di-chloro-naphthalene (β)-sulphonic chloride with PCl_5 (Widmann, *B.* 12, 962). Fine white needles. Insol. water, sl. sol. hot alcohol, v. sol. benzene.

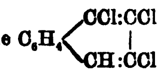
(ε)-Tri-chloro-naphthalene $C_{10}H_5Cl_3$. [65°]. From η-di-chloro-naphthalene by nitration and treatment of the resulting $C_{10}H_5Cl_2(NO_2)$ with PCl_5 (Clève, *Bl.* [2] 29, 500). Needles, v. sol. alcohol.

(θ)-Tri-chloro-naphthalene $C_{10}H_5Cl_3$. [76°]. From nitro-naphthalene ('α')-di-sulphonic acid and PCl_5 at 225° (Alén, *Bn.* II, 140). Small needles (from HOAc). V. sol. alcohol, m. sol. boiling HOAc.

('α')-Tri-chloro-naphthalene $C_{10}H_5Cl_3$. [82°].

Formation.—1. By the action of alcoholic KOH upon (α)-chloro-naphthalene-tetra-chloride (Faust a. Saame, *A.* 160, 71).—2. By heating (α)-naphthol-di-sulphonic chloride with PCl_5 (3 mols.) at 170°–180° (Claus a. Mielcke, *B.* 19, 1182).

Properties.—Colourless needles. V. sol. chloroform, ether, and hot alcohol. HNO_3 at 200° gives tri-chloro-nitro-phthalic acid (Widmann, *Bl.* [2] 28, 511).

('β')-Tri-chloro-naphthalene 

$$C_6H_4\left\langle\begin{matrix}CCl{:}CCl\\ |\\ CH{:}CCl\end{matrix}\right.$$

[90° uncor.]. (above 360°).

Formation.—1. By heating di-chloro-(α)-naphthol [101°], or sodium (α)-naphthol (β)-sulphonate with PCl_5 at 130°–140° (Claus a. Knyrim, *B.* 18, 2926).—2. By chlorinating (α)-nitro-naphthalene (Atterberg, *B.* 9, 926).

Properties.—Needles (from alcohol). May be sublimed. Insol. water, v. sol. other solvents.

Tri-chloro-naphthalene $C_{10}H_5Cl_3$. [90°]. Formed together with di-chloro-(β)-naphthol [125°], by heating sodium (β)-naphthol (β)-disulphonate with 5 mols. of PCl_5 at 210°.

Properties.—Fine white needles. Sublimable. V. sol. ether, benzene, etc., and hot alcohol, sl. sol. cold alcohol. Heated with nitric acid (S.G. 1·16), at 210° it yields a syrupy di-chloro-phthalic acid. By CrO_3 it is oxidised to the same di-chloro-phthalic acid, together with a tri-chloro-(α)-naphthoquinone which gives an anilide $C_{10}H_3Cl_2(NHPh)O_2$ which melts at [228°]. Hence it appears to be different from the tri-chloro-naphthalene of melting-point [90°] already known (Claus a. Schmidt, *B.* 19, 3174).

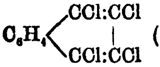
(γ)-Tri-chloro-naphthalene $C_{10}H_5Cl_3$. [103°]. Long white needles. Prepared by distillation of dichloro-naphthalene-(α)-sulphonic chloride with PCl_5 (Widmann, *B.* 12, 2230). Formed also by chlorinating (α)-nitro-naphthalene (Atterberg, *B.* 9, 317). Prisms. By heating to 170° with HNO_3 (1·42) it gives di-nitro-di-chloro-phthalic acid.

(η)-Tri-chloro-naphthalene $C_{10}H_5Cl_3$. [113°]. From nitro-naphthalene (β)-disulphonic chloride and PCl_5 at 190° (Alén, *Bn.* II, 140). Needles (from HOAc). V. sol. warm alcohol; v. e. sol. benzene. Volatile with steam.

(δ)-Tri-chloro-naphthalene $C_{10}H_5Cl_3$. [131°]. Formed by the action of PCl_5 on ('β')-di-nitro-naphthalene, nitro-(γ)-di-chloro-naphthalene, ('α') chloro-di-nitro-naphthalene [106°], ('β')-chloro-di-nitro-naphthalene, and nitro-('β')-di-chloro-naphthalene (Atterberg, *B.* 9, 1187, 1733; Widmann, *Bl.* [2] 28, 511). Long needles. Oxidation gives di-chloro-phthalic acid.

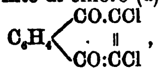
('α')-Tetra-chloro-naphthalene $C_{10}H_4Cl_4$. [130°]. Formed by the action of alcoholic KOH on the ('α')-di-chloro-naphthalene ('α')-tetra-chloride, obtained by chlorinating naphthalene (Faust a. Saame, *A.* 160, 72). Formed in the same way from ('β')-di-chloro-naphthalene tetra-chloride, and from ('β')-tri-chloro-naphthalene dichloride (Widmann, *Bl.* [2] 28, 511). Long needles. Oxidation gives di-chloro-phthalic acid.

Tetra-chloro-naphthalene $C_{10}H_4Cl_4$ *i.e.*



$$C_6H_4\left\langle\begin{matrix}CCl{:}CCl\\ |\\ CCl{:}CCl\end{matrix}\right.$$

(?). [140° uncor.]. Formed by heating (α)-naphthol-tri-sulphonic chloride with PCl_5 (4 mols.) at 210°–250°. Sublimes in colourless feathery needles. Crystallises from toluene in long thin needles. V. sol. hot alcohol, ether, chloroform, &c., sl. sol. cold alcohol, insol. water. On oxidation with CrO_3 or HNO_3 it is converted into di-chloro-(α)-naphthoquinone [189°],



$$C_6H_4\left\langle\begin{matrix}CO.CCl\\ \cdot\ \Vert\\ CO{:}CCl\end{matrix}\right.$$

, together with chlorinated phthalic acids (Claus a. Mielcke, *B.* 19, 1184).

Tetra-chloro-naphthalene $C_{10}H_4Cl_4$. [141°]. Formed by the action of alcoholic KOH on (γ)-di-chloro-naphthalene tetrachloride [85°], and on tri-chloro-naphthalene di-chloride [93°] (Atterberg a. Widmann, *B.* 10, 1842). Slender needles; sl. sol. alcohol. May be identical with the preceding.

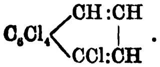
(ζ)-Tetra-chloro-naphthalene $C_{10}H_4Cl_4$. [160·5°]. Formed by acting on (ε)-di-chloro-di-nitro-naphthalene with PCl_5 (Alén, *Bl.* [2] 36, 435). Interlacing needles.

(γ)-Tetra-chloro-naphthalene $C_{10}H_4Cl_4$. [176°]. Obtained by the action of alcoholic KOH on ('α')-di-chloro-naphthalene ('α')-tetra-chloride got by chlorinating naphthalene (Widmann, *B.* 10, 1724; *Bl.* [2] 28, 512). Flat needles, sl. sol. alcohol.

(ε)-Tetra-chloro-naphthalene $C_{10}H_4Cl_4$. [180°]. From di-nitro-(γ)-di-chloro-naphthalene by distilling with PCl_5 (Atterberg a. Widmann, *B.* 10, 1843). Long needles; sl. sol. alcohol.

('β')-Tetra-chloro-naphthalene $C_{10}H_4Cl_4$. [194°]. Formed by chlorinating nitro-naphthalene (Atterberg, *B.* 9, 318). Needles, v. sl. sol. alcohol.

Penta-chloro-naphthalene $C_{10}H_3Cl_5$ *i.e.*

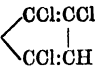


$C_6Cl_4\left\langle\begin{array}{l}CH:CH\\ \quad\;|\\ CCl:CH\end{array}\right.$. [169°]. (above 360°). Prepared by heating di-chloro-(α)-naphthoquinone with twice its weight of PCl_5 to 250° (Graebe, *A.* 149, 8; Claus a. Lippe, *B.* 16, 1016). Needles (from alcohol). On oxidation with fuming HNO_3 at 110° it gives tetra-chloro-naphthoquinone. Dilute HNO_3 at 190° gives tetra-chloro-phthalic acid.

('β')-Penta-chloro-naphthalene $C_{10}H_3Cl_5$. [177°]. From nitro-(δ)-tetra-chloro-naphthalene and PCl_5 (Atterberg a. Widmann, *B.* 10, 1843). Needles. Oxidises to tri-chloro-phthalic acid.

Hexa-chloro-naphthalene $C_{10}H_2Cl_6$. [143°]. Formed by chlorinating tri-chloro-naphthalene (Laurent). Six-sided columns; v. sl. sol. alcohol, m. sol. ether. May be oxidised to hexa-chloro-naphthoquinone.

(β)-Hepta-chloro-naphthalene



$C_6Cl_4\left\langle\begin{array}{l}CCl:CCl\\ \quad\;\;|\\ CCl:CH\end{array}\right.$ [194° uncor.]. Formed by heating tetra-chloro-(α)-naphthoquinone (1 pt.) with PCl_5 (2 pts.) for 6 or 8 hrs. at 250°. Small colourless needles. Sublimable. By heating with HNO_3 (1·5 S.G.) it is oxidised to penta-chloro-(α)-naphthoquinone [217°], and tetra-chloro-phthalic acid [250°] (Claus a. Wenzlik, *B.* 19, 1165; *cf.* Claus a. Lippe, *B.* 16, 1019)

Per-chloro-naphthalene $C_{10}Cl_8$. [203° uncor.]. (403°). Formed by heating tetra-chloro-oxy-naphthoquinone [265°], penta-chloro-(α)-naphthoquinone [217°], or (α)-naphthol-tri-sulphonic chloride, with PCl_5 at 250°. Prepared by the protracted chlorination of naphthalene in presence of $SbCl_5$ (Berthelot a. Jungfleisch, *Bl.* [2] 9, 446; *A. Ch.* [4] 15, 332). Colourless needles. Sublimable (Claus a. Wenzlik, *B.* 19, 1169; Claus a. Mielcke, *B.* 19, 1186). By heating with $SbCl_5$ at 290° it is split up into C_6H_6, C_2Cl_6, and CCl_4 (Ruoff, *B.* 9, 1048). It is partially converted into naphthalene by passing with hydrogen through a red-hot tube.

DI-CHLORO-NAPHTHALENE TETRA-BROMIDE $C_{10}H_6Cl_2Br_4$. [c. 100°]. From di-chloro-naphthalene and Br.

(α)-CHLORO-NAPHTHALENE TETRA-CHLORIDE $C_{10}H_7Cl_5$. [131°]. Formed by the action of Cl on naphthalene (Faust a. Saame, *A.* 160, 67) or on (α)-chloro-naphthalene (Widmann, *B.* 10, 1724; *Bl.* [2] 28, 505). Monoclinic prisms (from chloroform). Oxidation gives phthalic acid. Alcoholic KOH forms ('α')-tri-chloro-naphthalene.

(β)-Chloro-naphthalene tetra-chloride $C_{10}H_7Cl_5$. From (β)-chloro-naphthalene and Cl (W.). Oil.

Di-chloro-naphthalene tetra-chloride $C_{10}H_6Cl_6$. [85°]. From (γ)-di-chloro-naphthalene and Cl (Atterberg a. Widmann, *B.* 10, 1841). Prisms. Alcoholic KOH gives (δ)-tetra-chloro-naphthalene.

Di-chloro-naphthalene tetra-chloride $C_{10}H_6Cl_6$. [172°]. Formed by the action of Cl on ('α') or ('β')-di-chloro-naphthalene (Widmann, *Bl.* [2] 28, 506). Monoclinic prisms (from $CHCl_3$). V. e. sol. HOAc and benzene. Oxidation gives di-chloro-phthalic acid. Alcoholic KOH gives ('α') tetra-chloro-naphthalene.

Di-chloro-naphthalene tetra-chloride $C_{10}H_6Cl_6$. Formed, together with the preceding, by the union of Cl with ('α')-di-chloro-naphthalene. Oil. Alcoholic KOH gives (γ)-tetra-chloro-naphthalene.

('α')-Tri-chloro-naphthalene di-chloride $C_{10}H_7Cl_5$. [93°]. From (γ)-di-chloro-naphthalene and Cl (Atterberg a. Widmann, *B.* 10, 1842). Alcoholic KOH converts it into (δ)-tetra-chloro-naphthalene.

('β')-Tri-chloro-naphthalene di-chloride $C_{10}H_7Cl_5$ [152°]. Formed, together with $C_{10}H_7Cl_5HOAc$ [195°], by passing chlorine into a solution of (α)-chloro-naphthalene in glacial HOAc (Widmann, *Bl.* [2] 28, 507). Short prisms, sl. sol. alcohol.

CHLORO-NAPHTHALENE SULPHINIC ACID $C_{10}H_6Cl.SO_2H$. Formed by the action of sodium amalgam on (α)-chloro-naphthalene sulphonic bromide (?) [115°] obtained from bromo-naphthalene sulphonic acid by PCl_5 (Gessner, *B.* 9, 1504). Slender needles (from alcohol).—BaA'_2 1½aq.

(α)-CHLORO-NAPHTHALENE (α)-SULPHONIC ACID $C_{10}H_7ClSO_3$ *i.e.* $C_{10}H_6Cl(SO_3H)$ [1:4]. Obtained by heating (α)-diazo-(α)-naphthalene-sulphonic acid with HCl. V. sol. colourless tables (containing 2aq).

Salts.—A'K: silvery needles.—A'Na: thin scales.—A'Ag: thin tablets, v. sl. sol. cold water. A'_2Ba aq: sparingly soluble powder.

Ethyl ether A'Et: [46°]; large monosymmetrical prisms, *a*:*b*:*c* = 1·6785:1:?, β = 68° 58'.

Chloride $C_{10}H_6Cl(SO_2Cl)$: [95°]; large crystals (from chloroform).

Amide $C_{10}H_6Cl(SO_2NH_2)$: [226°]; sparingly soluble silvery scales (Clève, *B.* 20, 72).

(α)-Chloro-naphthalene (β)-sulphonic acid $C_{10}H_7ClSO_3$ *i.e.* $C_{10}H_6Cl(SO_3H)$ [1 : 2'or3']. Obtained by the action of Cu_2Cl_2 upon the diazo-compound of the naphthylamine sulphonic formed by reduction of the 'β'-nitro-naphthalene (β)-sulphonic acid (sparingly soluble Ba salt), which is one of the products of the nitration of naphthalene (β)-sulphonic acid.

Properties.—V. sol. colourless rhombic tables. When heated in a current of steam it yields (α)-chloro-naphthalene.

Salts.—A'Ag: thin glistening tables, sol. hot water, sl. sol. cold.—A'_2Ba aq: sparingly sol. crystalline powder.

Ethyl ether A'Et: [111°]; monosymmetrical crystals, *a*:*b*:*c* = ·4307:1:?, β = 86° 45'; v. e. sol. hot alcohol.

Chloride $C_{10}H_6Cl(SO_2Cl)$: [114°]; small scales.

Amide $C_{10}H_6Cl(SO_2NH_2)$: [216°]; thin plates (Clève, *B.* 20, 74).

(α)-Chloro-naphthalene *p*-sulphonic acid $C_{10}H_7ClSO_3$ *i.e.* $C_{10}H_6Cl(SO_3H)$ [1:4].

Formation.—1. By sulphonation of (α)-chloro-naphthalene (Zinin, *J. pr.* 33, 36).—2. From (α)-naphthylamine-*p*-sulphonic acid (naphthionic acid) by the action of Cu_2Cl_2 upon its diazo-compound.

Properties.—Silvery plates. Converted by Br into chloro-bromo-naphthalene [67°].

Salts. — KA'. — BaA'$_2$. — ZnA'$_2$ 6aq. — CuA'$_2$ 7aq.—AgA' aq (Arnell, *Bn.* ii. 153).

Ethyl ether EtA': [104°]; large thin monoclinic tables, a:b:c = 1·3281:1:1·1262, β = 80° 59'.

Chloride $C_{10}H_6Cl(SO_2Cl)$: [95°]; gives, with PCl_5, ('β')-di-chloro-naphthalene [68°] (Arnell, *Bl.* [2] 39, 62).

Amide $C_{10}H_6Cl(SO_2NH_2)$: [187°] (Cleve, *B.* 20, 73).

(α) - Chloro - naphthalene sulphonic acid $C_{10}H_6Cl.SO_3H$. Formed in small quantity, together with the preceding, by sulphonating chloronaphthalene with $Cl.SO_3H$ (Armstrong a. Williamson, *C. J. Proc.* 2, 234).

Chloride $C_{10}H_6Cl.SO_2Cl$: [127°]; short thick prisms.

(β) - Chloro - naphthalene sulphonic acid $C_{10}H_6Cl(SO_3H)$. Sparingly sol. water.

Formation.—1. By sulphonation of (β)-chloronaphthalene by H_2SO_4 or $ClSO_3H$ (Arnell, *Bl.* [2] 45, 184). It appears to be formed by isomeric change from the preceding by heating to 150° (Armstrong a. Wynne, *C. J. Proc.* 3, 22, 145). - 2. By the action of cuprous chloride upon diazotised (β)-naphthylamine-sulphonic acid obtained by treatment of (β)-naphthol sulphonic acid with NH_3.

Salts.—BaA'$_2$.—KA' ½aq.

Chloride $C_{10}H_6Cl(SO_2Cl)$: [110°]; needles; by distillation with PCl_5 it gives (ε)-di-chloro-naphthalene [136°].

Amide $C_{10}H_6Cl(SO_2NH_2)$: [184°]; needles (Forsling, *B.* 20, 80).

(β)-Chloro-naphthalene sulphonic acid $C_{10}H_6Cl.SO_3H$ [2:3']?

Formation.—1. By heating (β)-chloro-naphthalene with fuming H_2SO_4, and separated from the preceding acid through the greater solubility of its lead salt (Arnell, *Bl.* [2] 45, 184).—2. By diazotising (β)-naphthylamine sulphonic acid, and boiling with conc. HCl (Forsling, *B.* 19, 1715).

Properties. — Trimetric scales.—BaA'$_2$ 4aq: laminæ.—KA' aq: small scales.

Chloride [129°]. Converted by PCl_5 into di-chloro-naphthalene [61·5°].

Di-chloro-naphthalene (α)-sulphonic acid $C_{10}H_5Cl_2(SO_3H)$. Prepared by boiling the tetrachloride of (α)-naphthalene-sulphonic chloride with alcoholic KOH (Widmann, *B.* 12, 2228). Long flat needles. M. sol. cold water.

Salts.—A'K 2aq: fine needles.—A'Na aq: long flat prisms.—A'Ag 2aq: white needles.—A'$_2$Ca 4aq: slightly soluble leaflets.

Chloride [145°]. Scales or needles. Sol. benzene and hot acetic acid. By distillation with PCl_5 it gives (γ)-tri-chloro-naphthalene.

Amide [about 250°]. Flat feathery crystals.

Di-chloro-naphthalene (β)-sulphonic acid $C_{10}H_5Cl_2(SO_3H)$. Prepared by boiling the tetrachloride of naphthalene-(β)-sulphonic chloride ($C_{10}H_7(SO_2Cl)Cl_4$) with alcoholic KOH (Widmann, *B.* 12, 959). Readily sol. hot water, less in cold. Strong acid.

Salts.—A'K 5aq: very fine needles. S. 2·5 at 15°.—A'K 1½aq.—A'K 2½aq: small prisms.—A'Ag aq: crystalline powder.—A'$_2$Ba 4aq: fine sparingly soluble needles.—A'$_2$Ca 2aq.

Chloride [133°]; fine white needles. Sol. C_6H_6 and CS_2.

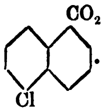
Amide [245°]; fine needles. Insol. water, sol. alcohol.

Tri- and Tetra-chloro-naphthalene sulphonic acids have been described by Laurent (*A.* 72, 299), but not sufficiently characterised.

CHLORO-NAPHTHALIC ACID *v.* CHLORO-OXY-(α)-NAPHTHOQUINONE.

CHLORO - NAPHTHOHYDROQUINONE *v.* CHLORO-HYDRO-NAPHTHOQUINONE.

CHLORO-(α)-NAPHTHOIC ACID $C_{10}H_6Cl(CO_2H)$, probably



. [245°].

Formation.—1. By chlorination of (α)-naphthoic acid in acetic acid solution.—2. By the action of cuprous chloride upon the diazo-compound obtained from nitro-(α)-naphthoic acid [239°].—3. From the nitrile.

Properties.—Sublimes in white needles. By fuming HNO_3 it is converted into chloro-nitro-(α)-naphthoic acid [225°] and chloro-di-nitro-naphthalene [175°] (Ekstrand, *B.* 17, 1604; 18, 2881).

Salt.—A'$_2$Ca 2aq: needles; S. ·86.

Ethyl ether A'Et: [42°]; quadratic tables.

Amide $C_{10}H_6Cl(CONH_2)$. [239°]. Formed by boiling the nitrile with alcoholic KOH (Ekstrand, *Bn.* ii. 925).

Nitrile $C_{10}H_6Cl.CN$ [145°]. White needles. Formed by chlorination of (α)-naphthonitrile (Ekstrand, *B.* 17, 1604).

Chloro-(β)-naphthoic acid $C_{10}H_6Cl.CO_2H$. [261°]. From the nitrile and fuming HCl at 150° (Ekstrand, *Bn.* ii. 931). Needles (from alcohol).

Ethyl ether EtA'. [45°]. Needles.

Nitrile $C_{10}H_6Cl.CN$. [138°]. From (β)-naphthonitrile in HOAc by chlorinating in presence of iodine.

Di-chloro-(β)-naphthoic acid $C_{10}H_5Cl_2.CO_2H$ [291° uncor.]. Sublimable. Colourless needles. Sparingly soluble in alcohol and in acetic acid. Formed by chlorination of (β)-naphthoic acid.

Salts.—A'$_2$Ca 2½aq: small sparingly soluble prisms.

Ethyl ether A'Et: [66°]; long needles. S. ·03 (Ekstrand, *B.* 17, 1605).

($\alpha_1\alpha_4$) CHLORO-NAPHTHOL $C_{10}H_6Cl(OH)$[1:4]. [57°]. Formed by the action of PCl_5 on (α)-naphthol-sulphonic acid. Small felted needles. On moderate oxidation it gives (α)-naphthoquinone, and by further oxidation phthalic acid (Claus a. Oehler, *B.* 15, 312).

Chloro-(α)-naphthol $C_{10}H_6Cl(OH)$. [109°]. Formed by distilling the compound $C_{10}H_8(HOCl)_2$ with aqueous HCl (Grimaux, *Bl.* [2] 18, 208). Slender needles.

(β)-Chloro-(α)-naphthol $C_{10}H_6Cl(OH)$[2:1] [c. 54°]. Is contained in the mother liquors obtained by passing chlorine into a solution of (α)-naphthol in HOAc (Cleve, *B.* 21, 894).

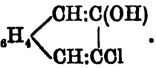
V. e. sol. most menstrua; only crystallisable from petroleum ether.

Chlorine forms di-chloro-naphthol [106°]. PCl_5 yields tri-chloro-naphthalene [92°].

Chloro-(β)-naphthol $C_{10}H_6Cl(OH)$[1:2]. [68°] (S.); [70°] (C.). Formed by the action of chlorine on (β)-naphthol sodium suspended in CS_2 (Schall, *B.* 16, 1901), or dissolved in HOAc (Cleve, *B.* 21, 895).

Needles or monoclinic plates (from chloroform); a:b:c = 1·96:1:1·956; β = 66° 54′. Volatile with steam. Converted by PCl_5 into chloronaphthyl phosphate $(C_{10}H_6Cl)_3PO_4$ [152°] or, at a higher temperature, into (1, 2)-di-chloronaphthalene [34°].

(2:3)-Chloro-(β)-naphthol

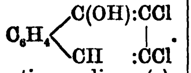


$C_6H_4<\begin{matrix}CH:C(OH)\\ |\\ CH:CCl\end{matrix}$.

[101° uncor.]. (308°). Formed by heating sodium (β)-naphthol (β)-sulphonate (Rumpf's acid) (1 mol.) with PCl_5 (2 mols.) at 150°-160°. Fine colourless needles. V. e. sol. alcohol, ether, etc., sl. sol water. Volatile with steam. By further action of PCl_5 it yields di-chloro-naphthalene [61°] (Claus a. Volz, *B.* 18, 3157).

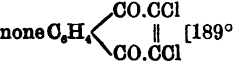
Chloro-(β)-naphthol $C_{10}H_6Cl.OH$. [115° uncor.]. Formed, together with (ε)-di-chloro-naphthalene, by heating potassium (β)-naphthol-sulphonate with PCl_5 (3 mols.) to 170° (Claus a. Zimmermann, *B.* 14, 1484). Fine needles or prisms. Sol. alcohol, ether, and hot water. Not volatile with steam.

Di-chloro-(α)-naphthol



$C_6H_4<\begin{matrix}C(OH):CCl\\ |\\ CH\ :CCl\end{matrix}$.

[101° uncor.]. Formed by heating sodium (α)-naphthol-(β)-sulphonate (1 mol.) with PCl_5 (2-2½ mols.) at 100°-120°. Sublimes in white needles. V. sol. ordinary solvents. By further treatment with PCl_5 it is converted into tri-chloro-naphthalene [90°]. By dilute HNO_3 at 200° it is oxidised to phthalic acid. By boiling with an acetic solution of CrO_3 it is oxidised to di-chloro-(α)-naphthoquinone



$C_6H_4<\begin{matrix}CO.CCl\\ \|\\ CO.CCl\end{matrix}$ [189°].

(Claus a. Knyrim, *B.* 18, 2926).

Di-chloro-(α)-naphthol $C_{10}H_5Cl_2(OH)$ [1:3:4]. [106°] (C.); [108°] (Zincke, *B.* 21, 1027). Formed by passing chlorine into a cold solution of (α)-naphthol in HOAc (Cleve, *B.* 21, 891). Needles. Sol. alcohol, chloroform, benzene. Crystallises from HOAc as $C_{10}H_5Cl_2OH + HOAc$ losing HOAc at 40°-50°.

Reactions.—1. Yields on heating a substance $C_{20}H_{10}Cl_2O_2$ (?).—2. Dilute HNO_3 forms yellow needles of a quinone-like substance and phthalic acid.—3. Oxidation with chromic acid forms chloro-naphthoquinone [116°], which on heating with aniline forms the anilide [203°] (*cf.* Knapp and Schultz, *A.* 210, 189).—4. PCl_5 forms (1,3,4) tri-chloro-naphthalene.

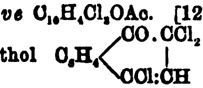
Acetyl derivative $C_{10}H_5Cl_2OAc$. [76°].

Di-chloro-(β)-naphthol $C_{10}H_5Cl_2(OH)$. [125° uncor.]. Formed, together with tri-chloro-naphthalene [90°], by heating sodium (β)-naphthol-(β)-di-sulphonate with PCl_5 at 210°. Colourless felted needles. Sublimable. V. sol. alcohol, ether, etc., sl. sol. hot water (Claus a. Schmidt, *B.* 19, 3174).

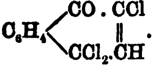
Tri-chloro-(α)-naphthol $C_{10}H_4Cl_3(OH)$[4:3:2:1]. [160°]. From tri-chloro-naphthol dichloride and $NaHSO_3$ (Zincke, *B.* 21, 1027). Silky needles (from HOAc). CrO_3 oxidises it to di-chloro-(α)-naphthoquinone.

Acetyl derivative $C_{10}H_4Cl_3OAc$. [124°].

Tri-chloro-(α)-naphthol



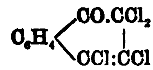
$C_6H_4<\begin{matrix}CO.CCl_2\\ |\\ CCl:CH\end{matrix}$ or



$C_6H_4<\begin{matrix}CO.CCl\\ \|\\ CCl_2.CH\end{matrix}$. *Tri-chloro-(α)-ketonaphthalene.*

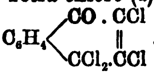
[121°]. From (α)-naphthol in HOAc by chlorination (Z.). Flat monoclinic prisms; v. e. sol. benzene. Boiling dilute alcohol converts it into chloro-(α)-naphthoquinone. Hydroxylamine hydrochloride appears to form an **oxim** [c. 148°], a compound $C_{10}H_5Cl_2(NO)$, and a third body [205°].

Tetra-chloro-(α)-naphthol



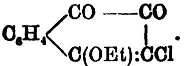
$C_6H_4<\begin{matrix}CO.CCl_2\\ |\\ CCl:CCl\end{matrix}$

or



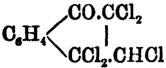
$C_6H_4<\begin{matrix}CO.CCl\\ \|\\ CCl_2.CCl\end{matrix}$. *Tetra-chloro-(α)-ketonaphthalene.*

Two modifications, corresponding perhaps to the above formulæ, are formed by chlorinating tri-chloro-(α)-naphthol (Z.), viz. rhombohedra [105°] and prisms [94°]. Boiling dilute alcohol or dilute HOAc convert both into di-chloro-(α)-naphthoquinone. Dilute alcoholic KOH forms chloro-oxy-naphthoquinone. KOH in absolute alcohol appears to form

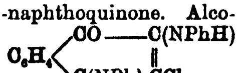


$C_6H_4<\begin{matrix}CO\ ——CO\\ |\\ C(OEt):CCl\end{matrix}$. [149°].

TRI-CHLORO-(α)-NAPHTHOL DICHLORIDE



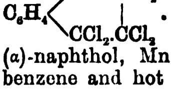
$C_6H_4<\begin{matrix}CO.CCl_2\\ |\\ CCl_2.CHCl\end{matrix}$. [157°]. From Cl and (α)-naphthol in cold HOAc (Zincke, *B.* 21, 1027). Monoclinic plates (from benzene). $NaHSO_3$ in presence of HOAc reduces it to tri-chloro-(α)-naphthol. Dilute alcohol or dilute HOAc at 130° form di-chloro-(α)-naphthoquinone. Alcoholic aniline forms



$C_6H_4<\begin{matrix}CO——C(NPhH)\\ \|\\ C(NPh).CCl\end{matrix}$

[157°] whence $B'_2H_2PtCl_6$.

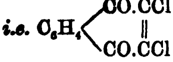
Tetra-chloro-(α)-naphthol dichloride



$C_6H_4<\begin{matrix}CO\ .\ CCl_2\\ |\\ CCl_2.CCl_3\end{matrix}$. [130°]. From tetra-chloro-(α)-naphthol, MnO_2, and HCl (Z.). V. sol. benzene and hot alcohol, sl. sol. ether. Does not react with aniline. May be reduced to tri-chloro-(α)-naphthol. Alcoholic KOH forms $CCl_2:CCl.CO.C_6H_4.CO_2H$ [128°].

CHLORO-(α)-NAPHTHOQUINONE $C_{10}H_5ClO_2$

i.e.



$C_6H_4<\begin{matrix}CO.CCl\\ \|\\ CO.CCl\end{matrix}$ [111°] (P.); [116°] (Clève, *B.* 21, 891); [118°] (Zincke, *B.* 21, 1027). A by-product in the preparation of di-chloro-(α)-naphthoquinone [189°] by treating di-nitro-(α)-naphthol with $KClO_3$ and HCl (Plagemann, *B.* 15, 485).

The following amides are formed by treating di-chloro-(α)-naphthoquinone with the corresponding amine in alcoholic solution (P.):

Methylamide $C_{10}H_4ClO_2NMeH$. [150°]. Orange needles, v. sol. alcohol.

Di-methyl-amide $C_{10}H_4ClO_2NMe_2$. [85°]. Scarlet needles, v. sol. alcohol.

Ethylamide $C_{10}H_4ClO_2NEtH$. [110°]. Brownish-red needles, v. sol. alcohol.

Anilide $C_{10}H_4ClO_2.NHC_6H_5$ [208°] (P.); [202°] (K. a. S.; C.). Red metallic needles. Sol.

acetic acid and alkalis, sl. sol. alcohol. Its solution in conc. H_2SO_4 is of a magenta colour. $SnCl_2$ reduces it to a dihydride [170°] (Knapp a. Schultz, *A.* 210, 189).

Nitrosamine $C_{10}H_4ClO_2N(NO)C_6H_5$: [126°]; yellow needles or plates, sol. benzene, sl. sol. ligroïn; formed by passing nitrous acid into the anilide suspended in acetic acid (Plagemann, *B.* 16, 895).

p-Bromo-anilide $C_{10}H_4ClO_2.NHC_6H_4Br$. [262°]. Formed by bromination of chloro-naphthoquinone-anilide; or by the action of *p*-bromaniline on di-chloro-naphthoquinone. Sol. in NaOH to a red solution, sl. sol. alcohol and acetic acid.

m-Nitro-anilide $C_{10}H_4ClO_2.NHC_6H_4(NO_2)$. [215°]. Formed by the action of *m*-nitraniline on di-chloro-naphthoquinone. Yellowish-red sparingly soluble needles.

p-Nitro-anilide $C_{10}H_4ClO_2.NH.C_6H_4(NO_2)$. [282°]. Formed by the action of *p*-nitraniline on di chloro-naphthoquinone; or by nitration of chloro-naphthoquinone-anilide. Red felted needles. Sl. sol. alcohol and acetic acid, sol. alkalis to a violet solution. *Nitrosamine* $C_{10}H_4ClO_2N(NO)C_6H_4(NO_2)$. [126°].

o-Toluide $C_{10}H_4ClO_2.NHC_6H_3(CH_3)H$. [152°]. Red metallic crystals. Formed by the action of *o*-toluidine on di-chloro-naphthoquinone.

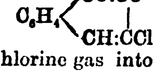
p-Toluide $C_{10}H_4ClO_2.NHC_6H_4(CH_3)$. [196°]. Formed by the action of *p*-toluidine on di-chloro-naphthoquinone. Metallic red crystals. Sol. acetic acid, sl. sol. alcohol. Dissolves in NaOH to a violet solution.

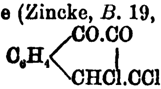
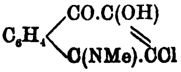
Bromo-o-toluide $C_{10}H_4ClO_2.NHC_6H_3(CH_3)Br$. [212°]. Formed by bromination of chloro-naphthoquinone-*o*-toluide. Sl. sol. alcohol and acetic acid.

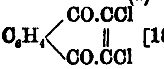
Bromo-p-toluide $C_{10}H_4ClO_2.NHC_6H_3(CH_3)Br$. [185°]. Formed by bromination of chloro-naphthoquinone-*p*-toluide. Red needles. Sl. sol. alcohol, dissolves in NaOH to a violet solution.

Nitro-o-toluide $C_{10}H_4ClO_2.NH.C_6H_3(CH_3)(NO_2)$. [230°]. Formed by nitrating the *o*-toluide (P.).

Nitro-p-toluide $C_{10}H_4ClO_2.NHC_6H_3(CH_3)(NO_2)$. [236°-240°]. Formed by nitration of chloro-naphthoquinone-*p*-toluide. Red felted needles. Sl. sol. alcohol and acetic acid. Dissolves in NaOH to a violet solution.

Chloro-(β)-naphthoquinone  $C_6H_4<\begin{matrix}CO.CO\\ |\\ CH:CCl\end{matrix}$ [172°]. Obtained by passing chlorine gas into (β)-naphthoquinone suspended in ten times its weight of acetic acid. Red needles. Sol. hot alcohol, acetic acid, benzene, and chloroform. Dissolves in dilute caustic alkalis with a reddish-brown colour forming chloro-oxy-(α)-naphthoquinone. With alcoholic NH_3 or aniline it yields respectively the imide or anilide of chloro-oxy-(α)-naphthoquinone (Zincke, *B.* 19, 2497).

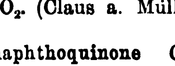
Dichloride  $C_6H_4<\begin{matrix}CO.CO\\ |\\ CHCl.CCl_2\end{matrix}$. [128°]. Formed by passing chlorine into a solution of (β)-naphthoquinone in HOAc (Zincke, *B.* 20, 2890). Thin needles (containing 2aq). In the hydrated condition it melts at 112°. Methylamine forms  $C_6H_4<\begin{matrix}CO.C(OH)\\ \|\\ C(NMe).CCl\end{matrix}$ [200°].

Di-chloro-(α)-naphthoquinone $C_{10}H_6Cl_2O_2$ *i.e.*  $C_6H_4<\begin{matrix}CO.CCl\\ \|\\ CO.CCl\end{matrix}$ [189°].

Formation.—1. From chloro-naphthalene tetrachloride $C_{10}H_7Cl_5$ and boiling HNO_3 (Laurent, *A. Ch.* [2] 74, 35; *Rev. Scient.* 13, 591).—2. From di-nitro-naphthol, $KClO_3$ and HCl (Graebe, *A.* 149, 3).—3. From naphthalene in HOAc and CrO_2Cl_2 (Carstanjen, *B.* 2, 633).—4. Together with chlorinated phthalic acids by oxidation of tetra-chloro-naphthalene [140°] (from (α)-naphthol-tri-sulphonic chloride and PCl_5) with CrO_3 or HNO_3.

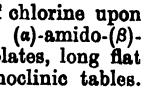
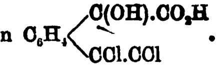
Properties.—Sublimes in yellow needles. Insol. water, sl. sol. cold alcohol and ether. By alkalis it is converted into chloro-oxy-(α)-naphthoquinone which forms yellow needles [215°]. With aniline it yields $C_{10}H_4Cl(NHPh)O_2$, splendid violet-red crystals [203° uncor.] (Claus a. Mielcke, *B.* 19, 1184). Oxidation gives phthalic acid. PCl_5 forms penta-chloro-naphthalene.

Di-chloride $C_{10}H_4Cl_4O_2$. [117° uncor.]. Formed by heating di-chloro-(α)-naphthoquinone (10 pts.) with HCl of S.G. 1·2 (48 pts.) and MnO_2 (10 pts.) for 10 hours at 230°. Large colourless prisms. Sublimes unaltered. By $SnCl_2$ or other reducing agent it is re-converted into di-chloro-(α)-naphthoquinone (Claus, *B.* 19, 1142).

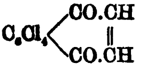
('β')-Di-chloro-(α)-naphthoquinone $C_{10}H_4Cl_2O_2$ probably  $C_6H_3Cl<\begin{matrix}CO.CCl\\ \|\\ CO.CH\end{matrix}$ [149° uncor.]. Formed, together with chloro-phthalic acid $C_6H_3Cl(CO_2H)_2$ [4:2:1], by oxidation of (ε)-di-chloro-naphthalene in acetic acid solution by CrO_3. Yellow needles. Sublimable without decomposition. Dissolves in aqueous KOH with a red colour. By boiling with alkalis it is converted into ('β')-chloro-oxy-naphthoquinone $C_{10}H_4Cl(OH)O_2$. (Claus a. Müller, *B.* 18, 3073).

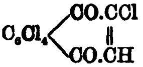
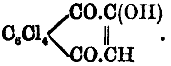
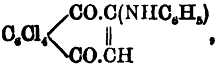
Di-chloro-(α)-naphthoquinone $C_{10}H_4Cl_2O_2$. [153°]. Formed, together with the isomeride [189°] by chlorinating di-nitro-naphthol (P.).

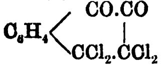
p-**Di-chloro-(α)-naphthoquinone** $C_{10}H_4Cl_2O_2$. [174°]. Formed, together with di-chloro-phthalide, by oxidation of di-chloro-naphthalene [68°] with CrO_3 and glacial acetic acid. Long yellow needles. Sublimable. Sol. alcohol and ether, nearly insol. water. By NaOH it is converted into chloro-oxy-(α)-naphthoquinone. With aniline it forms $C_{10}H_4Cl(NHPh)O_2$, garnet red needles, [185°] (Guareschi, *B.* 19, 1155).

Di-chloro-(β)-naphthoquinone  $C_6H_4<\begin{matrix}CO.CO\\ |\\ CCl:CCl\end{matrix}$ [184°]. Formed by the action of chlorine upon (β)-naphthoquinone or better (α)-amido-(β)-naphthol in acetic acid. Red plates, long flat needles, thick rhombic or monoclinic tables. Sol. chloroform, sl. sol. alcohol. Sublimable. With alcoholic NH_3 or aniline it yields the imide or anilide of chloro-oxy-(α)-naphthoquinone. It dissolves in cold dilute NaOH to a colourless solution forming an acid $C_{10}H_6Cl_2O_3$ which possibly has the constitution  $C_6H_4\left\langle\begin{array}{l}C(OH).CO_2H\\ \\ CCl.CCl\end{array}\right.$. (Zincke, *B.* 19, 2499). This acid crystallises in slender needles (containing aq) [100°]; it forms a *methyl-ether* $C_{10}H_4Cl_2(OH).CO_2Me$ [138°] and an *acetyl-methyl ether* $C_{10}H_4Cl_2(OAc)CO_2Me$ [76°].

Tri-chloro-(α)-naphthoquinone $C_6H_3Cl_3O_2$. Formed by oxidation of tri-chloro-naphthalene [90°] (from (β)-naphthol-(β)-di-sulphonic acid and PCl_5) with CrO_3 and acetic acid. It was not isolated, but by treatment with aniline was converted into the anilide $C_{10}H_4Cl_2(NHPh)O_2$, which formed reddish-violet plates [228°] uncor., sublimable (Claus a. Schmidt, *B.* 19, 3177).

Tetra-chloro-(α)-naphthoquinone  $C_6Cl_4\left\langle\begin{array}{l}CO.CH\\ \quad\Vert\\ CO.CH\end{array}\right.$ [160° uncor.]. Long yellow needles. Sublimable. Prepared by oxidation of penta-chloro-naphthalene with fuming HNO_3 at 110°. PCl_5 converts it into hepta-chloro-naphthalene (Claus a. Lippe, *B.* 16, 1018).

Penta-chloro-(α)-naphthoquinone  $C_6Cl_4\left\langle\begin{array}{l}CO.CCl\\ \quad\Vert\\ CO.CH\end{array}\right.$ [217° uncor.]. Formed together with tetra-chloro-phthalic acid, by oxidation of hepta-chloro-naphthalene [194°] with HNO_3 (1·5 S.G.) at 100°. Glistening golden plates (from chloroform). Sublimes in long glistening needles. By alkalis it is converted into salts of tetra-chloro-oxy-naphthoquinone  $C_6Cl_4\left\langle\begin{array}{l}CO.C(OH)\\ \quad\Vert\\ CO.CH\end{array}\right.$. With aniline it yields  $C_6Cl_4\left\langle\begin{array}{l}CO.C(NHC_6H_5)\\ \quad\Vert\\ CO.CH\end{array}\right.$, which crystallises from alcohol or acetic acid in glistening red plates [240° uncor.]. By heating with PCl_5 at 250° it is converted into per-chloro-naphthalene [203°] (Claus a. Wenzlik, *B.* 19, 1166).

DI-CHLORO-(β)-NAPHTHOQUINONE DICHLORIDE  $C_6H_4\left\langle\begin{array}{l}CO.CO\\ \quad\vert\\ CCl_2.CCl_2\end{array}\right.$ [91°]. Formed by passing chlorine into a solution of (1, 2)-amido-naphthol in HOAc (Zincke, *B.* 21, 495). Yellowish crystals (from ether); v. sol. ether, HOAc, and petroleum ether.

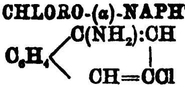
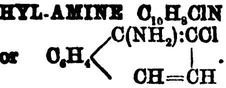
DI-CHLORO-(α)-NAPHTHOQUINONE SULPHONIC ACID $C_{10}H_3Cl_2O_2(SO_3H)$[2:3:1:4:3′]. From sodium di-nitro-(α)-naphthol sulphonate ((α)-*naphthol yellow*), $KClO_3$ and HCl (Claus, *J. pr.* [2] 37, 181). Light yellow plates, v. sol. water and alcohol, insol. ether. Converted by potash-fusion into (β)-oxy-phthalic acid. Aniline forms $C_{10}H_3Cl(NPhH)O_2(SO_3H)$ [190°], a colouring matter crystallising in dark-red plates.

Salts.—NaA′: yellow crystalline powder (from water) or yellow plates (from alcohol).—CaA'_2.—BaA'_2.

DI-CHLORO-NAPHTHOSTYRIL *v.* DI-CHLORO-AMIDO-NAPHTHOIC LACTAM.

TETRA-CHLORO-(ββ)-DINAPHTHYL $C_{20}H_{10}Cl_4$. Amorphous (Smith a. Poynting, *C. J.* 27, 854).

Hexa-chloro-(αα)-dinaphthyl $C_{20}H_8Cl_4$. Amorphous (Lossen, *A.* 144, 77).

CHLORO-(α)-NAPHTHYL-AMINE $C_{10}H_8ClN$ *i.e.*  $C_6H_4\left\langle\begin{array}{l}C(NH_2){:}CH\\ \qquad\quad\vert\\ \quad CH{=}CCl\end{array}\right.$ or  $C_6H_4\left\langle\begin{array}{l}C(NH_2){:}CCl\\ \qquad\quad\vert\\ \quad CH{=}CH\end{array}\right.$. [56°]. Obtained by reduction of di-chloro-(α)-naphthylamine [82°] with tin and HCl. Thin white needles. Very unpleasant smell. Sl. sol. hot water. Very volatile with steam. Its salts are decomposed by water.

Salts. — B′HCl aq: silky needles. — $B'HClSnCl_2$: thin glistening plates. —$B'H_2SO_4aq$: slender white needles (Clève, *B.* 20, 450).

Chloro-(α)-naphthylamine $C_{10}H_6Cl(NH_2)$. [86°]. From chloro-nitro-naphthalene by reduction (Atterberg, *B.* 10, 548).—B′HCl.

Chloro-(α)-naphthylamine $C_{10}H_6Cl(NH_2)$. [94°]. Formed by reducing (γ)-di-chloro-nitro-naphthalene (Atterberg, *B.* 9, 1730). Fe_2Cl_6 gives a greyish-green coloration. Displacement of NH_2 by Cl forms (ζ)-di chloro-naphthalene (Atterberg, *B.* 10, 548).—B′HCl aq.—$B'HSnCl_3$.—$B'H_2SO_4$.

Chloro-(α)-naphthylamine $C_{10}H_6Cl(NH_2)$. [98°]. Formed by the slow action of $SnCl_4$ on a solution of (α)-naphthylamine hydrochloride exposed to air (Seidler, *B.* 11, 1201).

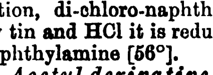
Acetyl derivative $C_{10}H_6Cl(NHAc)$. [184°].

(α)-Chloro-(β)-naphthylamine $C_{10}H_6Cl.NH_2$ [1:2]. [59°]. From the acetyl derivative and HCl. Elimination of NH_2 gives (α)-chloro-naphthalene.—B′HCl aq.

Acetyl derivative $C_{10}H_6Cl.NHAc$. [147°]. Formed by passing chlorine into a solution of acetyl (β)-naphthylamine in dilute HOAc (Clève, *B.* 20, 1989).

Di-chloro-(α)-naphthylamine $C_{10}H_5Cl_2(NH_2)$. [104°]. Formed by reducing ('β')-di-chloro-nitro-naphthalene [68°]. Needles (from alcohol). B′HCl.—$B'HSnCl_3$.—$B'_2H_2PtCl_6$ 2aq.—$B'H_2SO_4$.

(η)-Di-chloro-naphthylamine $C_{10}H_5Cl_2(NH_2)$. [94° ?]. Formed by reducing (η)-di-chloro-nitro-naphthalene (Clève, *Bl.* [2] 29, 500).—B′HCl.

Di-chloro-(α)-naphthylamine $C_{10}H_7Cl_2N$ probably  $C_6H_4\left\langle\begin{array}{l}C(NH_2){:}CCl\\ \qquad\quad\vert\\ \quad CH{=}CCl\end{array}\right.$. [82°]. Obtained by saponifying its acetyl derivative, which is formed by passing chlorine (2 mols.) into an acetic acid solution of acetyl-(α)-naphthylamine (1 mol.). Crystalline solid, of disagreeable odour. V. e. sol. alcohol. Volatile with steam. Non-basic. By HNO_3 it is oxidised to phthalic acid. By elimination of the NH_2 group by the diazo-reaction, di-chloro-naphthalene [61°] is formed. By tin and HCl it is reduced to mono-chloro-(α)-naphthylamine [56°].

Acetyl derivative $C_{10}H_5Cl_2.NHAc$: [214°]; long thin white needles; sol. acetic acid, alcohol and chloroform; sublimable (Clève, *B.* 20, 448).

DI-CHLORO-DI-(β)-NAPHTHYL-AMINE $(C_{10}H_6Cl)_2NH$.

Benzoyl derivative $(C_{10}H_6Cl)_2NBz$. [203° uncor.]; small white needles; sol. alcohol, benzene, and chloroform. Formed by the action of PCl_5 on the benzoyl derivative of di-(β)-naphthylamine (Claus a. Richter, *B.* 17, 1590).

DI-CHLORO-NAPHTHYLENE-DIAMINE $C_{10}H_4Cl_2(NH_2)_2$. [205°]. Formed by reduction of di-chloro-di-nitro-naphthalene [253°] by tin HCl, and HOAc (Alén, *Bl.* [2] 36, 435).

DI-CHLORO (α)-DINAPHTHYLENE-OXIDE $C_{20}H_{10}Cl_2O$. [151°]. Prepared by the action of PCl_5 on (α)-dinaphthylene-oxide (Knecht a. Unzeitig, *B.* 13, 1725). Sublimes and crystallises in yellow needles. V. sol. benzene and acetic acid, sl. sol. alcohol, ether, and chloroform.

Di-chloro-(β)-dinaphthylene-oxide $C_{20}H_{10}Cl_2O$. [245°]. Prepared by the action of PCl_5 on (β)-dinaphthylene-oxide (K. a. U.). Yellow glistening needles (from benzene).

TRI-CHLORO- (α) and (β) -DI-NAPHTHYL-ETHANE $CCl_3.CH(C_{10}H_7)_2$. Formed together by the action of H_2SO_4 on a mixture of naphthalene and chloral, thus: $CCl_3.CH.O + 2C_{10}H_8 = CCl_3.CH(C_{10}H_7)_2 + H_2O$.

Preparation.—6 pts. of H_2SO_4 mixed with 6 pts. of fuming H_2SO_4 are added to a mixture of 3 pts. of chloral, 8 pts. of naphthalene, and 6 pts. of chloroform (Grabowski, *B.* 11, 298).

(β)-*modification* [156°]. Crystals. Insol. cold, sl. sol. hot, alcohol and ether. Separated from the (α)-modification by its sparing solubility in alcohol. On distillation it loses HCl forming dichloro-(β)-dinaphthyl-ethylene.

Tetra-nitro-derivative [258°]. Yellow powder. Insol. alcohol, ether, C_6H_6, &c.

(α)-*modification.* Not isolated in the pure state. V. sol. alcohol.

DI-CHLORO-(α)-DI-NAPHTHYL-ETHYLENE $CCl_2{:}CH(C_{10}H_7)_2$. [150°]. Sl. sol. cold, v. sol. hot, alcohol. Long colourless needles. Less stable than the (β)-modification. Prepared by distilling crude trichloro-(α)-di-naphthyl-ethane with 20 p.c. of lime (Grabowski, *B.* 11, 299).

Tetra-nitro-derivative. [214°].

Di-chloro-(β)-di-naphthyl-ethylene $CCl_2{:}CH(C_{10}H_7)_2$. [219°]. (above 360°). Distils without decomposition. Short prismatic pillars. Sl. sol. alcohol. Prepared by the distillation of tri-chloro-(β)-di-naphthyl-ethane.

Tetra-nitro-derivative. [293°] (Grabowski, *B.* 11, 299).

CHLORO - (β) - NAPHTHYL - PHOSPHORIC ACID $C_{10}H_6Cl.OPO(OH)_2$. [205° uncor.]. Formed as a by-product in the action of PCl_5 (2 mols) on potassium (β)-naphthol-sulphonate (1 mol.) at 150° (Claus a. Zimmermann, *B.* 14, 1483). Small plates. By boiling alkalis it is decomposed into chloro-(β)-naphthol and phosphate.

CHLORO-NICOTINIC ACID *v.* Chloro-pyridine-carboxylic acid.

ω-DI-CHLORO-*o*-NITRO-ACETOPHENONE. $C_6H_4(NO_2).CO.CHCl_2$. [73°]. *Nitro-phenyl di-chloro-methyl ketone.* Formed by chlorination of $C_6H_4(NO_2).CO.Me$ (Gevekoht, *A.* 221, 328). Plates (from benzoline).

CHLORO-NITRO-AMIDO-PHENOL $C_6H_5ClN_2O_3$ *i.e.* $C_6H_2Cl(NO_2)(NH_2)(OH)$ [2:4:6:1]. [160°]. Formed by reducing chloro-di-nitro-phenol [110°] with ammonium sulphide (Griess a. Kolbe, *A.* 109, 286; Faust a. Miller, *A.* 173, 315; *Z.* 1871, 339; Armstrong, *C. J.* 25, 14). Slender brass-yellow needles (containing ½ aq) (from hot water). When dried at 100° it is scarlet. Elimination of NH_2 gives chloro-nitro-phenol [110°].—$B'HCl$: yellowish needles.—$B'_2H_2SO_4$.—$NH_4(C_6H_4ClN_2O_3)$.—$Ba(C_6H_4ClN_2O_3)_2$ 4aq: slender black needles.

Chloro-nitro-amido-phenol. *Methyl ether* $C_6H_2(Cl)(NO_2)(OMe)(NH_2)$. *Chloro-nitro-anisidine.* *Acetyl derivative* [185°], yellow needles, sol. alcohol and ether, insol. cold water (Herold, *B.* 15, 1686).

Chloro-di-nitro-amido-phenol. *Methyl ether* $C_6H(Cl)(NO_2)_2(OMe)(NH_2)$. Acetyl derivative [165°], yellow needles (H.).

Chloro-tri-nitro-amido-phenol. *Methyl ether* $C_6(Cl)(NO_2)_3(OMe)(NH_2)$. Acetyl derivative [198°], orange-yellow needles (H.).

CHLORO - NITRO - AMIDO - DI - PHENYL - AMINE *v.* Chlornitrophenyl-phenylene-diamine.

CHLORO-NITRO-ANILINE $C_6H_3Cl(NO_2)(NH_2)$ [4:3:1]. [103° uncor.].

Formation.—1. By nitration of *p*-chloro-aniline dissolved in 10 pts. of H_2SO_4; the yield is 50 p.c. of the chloraniline.—2. Together with a much larger quantity of the (6:3:1)-isomeride by reduction of chloro-di-nitro-benzene $C_6H_3Cl(NO_2)_2$ [4:3:1] in alcoholic solution with $SnCl_2$ and HCl.

Properties.—Small yellow glistening needles (from hot petroleum-ether), or long thin needles (from boiling water). V. sol. alcohol, ether and chloroform, m. sol. hot water, nearly insol. cold water. Weak base. By elimination of the NH_2 group it gives *o*-chloro-nitro-benzene [33°]. By replacement of the NH_2 group by Cl, di-chloro-nitro-benzene [55°] is formed.

Acetyl derivative $C_6H_3Cl(NO_2)(NHAc)$ [100°]; small yellow needles (Claus a. Stiebel *B.* 20, 1379).

Chloro-nitro-aniline $C_6H_3Cl(NO_2)(NH_2)$ [2:4:1]. [105°]. Prepared by heating (1, 2, 4)-di-chloro-nitro-benzene [43°] with ammonia at 210° (Beilstein a. Kurbatoff, *A.* 182, 98). Appears also to be formed in small quantity by nitrating acetyl-*o*-chloro-aniline. Light yellow needles. Elimination of NH_2 gives *m*-chloro-nitro-benzene.

Acetyl derivative $C_6H_3Cl(NO_2)(NHAc)$. [139°].

Chloro-nitro-aniline $C_6H_3Cl(NO_2)(NH_2)$ [4:2:1]. [115°]. (B. a. K.); [116°] (K.). From (1,4,2)-di-chloro-nitro-benzene and alcoholic NH_3 at 165°. Formed also by nitrating acetyl *p*-chloro-aniline (Körner, *G.* 4, 373; Beilstein a. Kurbatoff, *B.* 9, 633; *A.* 182, 94). Orange-yellow needles (from water) or spherical groups of brick-red needles (from alcohol). Elimination of NH_2 gives *m*-chloro-nitro-benzene. Reduction to chloro-phenylene-diamine followed by treatment with sodium-amalgam gives *o*-phenylene-diamine (Körner).

Chloro-nitro-aniline $C_6H_3Cl(NO_2)(NH_2)$ [6:3:1]. [117°].

Formation.—1. Together with a smaller quantity of the (4:3:1)-isomeride by reduction of chloro-di-nitro-benzene $C_6H_3Cl(NO_2)_2$ [4:3:1] in alcoholic solution with $SnCl_2$ (Claus a. Stiebel, *B.* 20, 1379).—2. By nitration of acetyl-*o*-chloro-aniline (B. a. K.).

Properties.—Yellow needles. Elimination of NH_2 gives *p*-chloro-nitro-benzene.

Acetyl derivative $C_6H_3Cl(NO_2)(NHAc)$. [154°].

Chloro-nitro-aniline $C_6H_3Cl(NO_2)(NH_2)$ [3:6:1]. [125°].

Formation.—1. By heating (3,6,1)-di-chloro-nitro-benzene [33°] with alcoholic NH_3 for 10 hours at 160° (Körner, *G.* 4, 373).—2. From chloro-di-nitro-benzene [59°] and NH_3 (Laubenheimer, *B.* 9, 1826).—3. By nitrating acetyl *m*-chloro-aniline (B. a. K.).

Properties.—Thin yellow laminæ (from alcohol). Elimination of NH_2 gives *p*-chloro-nitro-benzene. Reduction by tin and HCl gives chloro-phenylene-diamine whence sodium-amalgam produces *o*-phenylene-diamine (Körner).

Acetyl derivative $C_6H_3Cl(NO_2)(NHAc)$. [115°].

Chloro-nitro-aniline $C_6H_3Cl(NO_2)(NH_2)$ [3:4:1]. [157°]. Formed, together with the preceding, by nitrating acetyl *m*-chloro-aniline (B. a. K.). Yellow laminæ (from benzene). Elimination of NH_2 gives *o*-chloro-nitro-benzene [32·5°].

Acetyl derivative [142°].

Chloro-di-nitro-aniline $C_6H_2Cl(NO_2)_2(NH_2)$ [4:2:6:1]. [145°]. From di-chloro-di-nitro-benzene [104°] and alcoholic NH_3. Formed also by chlorinating di-nitro-aniline [138°] and by treating the methyl ether of chloro-di-nitro-phenol [65°] with NH_3 (Körner). Orange needles. Alcoholic KOH converts it into chloro-di-nitro-phenol.

Di-chloro-nitro-aniline $C_6H_2Cl_2(NO_2)(NH_2)$ [3:6:2:1]. [68°]. From its acetyl derivative, which is formed, together with the (3,6,4,1)-isomeride [153°], by the nitration of $C_6H_3Cl_2(NHAc)$ [3:6:1] (Beilstein a. Kurbatow, *A.* 192, 232). Also from (3,6,2,1)-di-chloro-di-nitro-benzene and alcoholic NH_3 (Körner). Yellow needles. Displacement of NH_2 by Cl gives (3,6,1,2)-tri-chloro-nitro-benzene [89°].

Acetyl derivative $C_6H_2Cl_2(NO_2)(NHAc)$. [205°].

Di-chloro-nitro-aniline $C_6H_2Cl_2(NO_2)(NH_2)$ [3:5:6:1]. [79°]. Prepared together with the (3,5,4,1)-isomeride [171°] by nitration of acetyl-(1,3,5)-di-chloro-aniline. Yellow needles. Converted by elimination of NH_2 into di-chloro-nitro-benzene [33°].

Acetyl derivative [139°]. Sol. CS_2 (Beilstein a. Kurbatow, *B.* 11, 1979).

Di-chloro-nitro-aniline $C_6H_2Cl_2(NO_2)(NH_2)$ [4:3:2:1]. [96°]. Prepared together with the (4,3,6,1)-isomeride [175°] by nitration of acetyl-(4,3,1)-di-chloro-aniline. Yellow needles.

Acetyl derivative [153°] (Beilstein a. Kurbatow, *B.* 11, 1978).

Di-chloro-*o*-nitro-aniline $C_6H_2Cl_2(NO_2)(NH_2)$ [2:4:6:1]. [99°]. Formed by passing chlorine into a solution of *o*-nitraniline in conc. HCl (Langer, *A.* 215, 111). Formed also by nitration of acetyl-(4,2,1)-di-chloro-aniline, or by chlorination of acetyl-(4,2,1)-chloro-nitro-aniline, and decomposition of the resulting acetyl derivative by HCl (Witt, *B.* 7, 1603; 8, 820). Slender orange needles (from benzoline). V. sol. alcohol, ether, or benzoline. Elimination of NH_2 gives di-chloro-nitro-benzene [65°]

Acetyl derivative $C_6H_2Cl_2(NO_2)(NHAc)$. [188°].

Di-chloro-nitro-aniline $C_6H_2Cl_2(NO_2)(NH_2)$ [3:6:4:1]. [153°]. Prepared, together with the (3,6,2,1)-isomeride [68°], by nitration of acetyl-(3,6,1)-di-chloro-aniline. Yellow needles.

Acetyl derivative [146°] (Beilstein a. Kurbatow, *B.* 11, 1978; *A.* 196, 235).

Di-chloro-nitro-aniline $C_6H_2Cl_2(NO_2)(NH_2)$ [3:2:6:1]. [163°]. Formed by heating $C_6H_2Cl_3(NO_2)$ [56°] with alcoholic NH_3 at 210° (Beilstein a. Kurbatow, *A.* 192, 235). By elimination of NH_2 it gives di-chloro-nitro-benzene [43°].

Di-chloro-nitro-aniline $C_6H_2Cl_2(NO_2)(NH_2)$ [3:5:4:1]. [171°]. Large yellow needles. Prepared, together with the (3,5,6,1)-isomeride [79°], by nitration of acetyl-(5,3,1)-di-chloro-aniline. Elimination of NH_2 gives di-chloro-nitro-benzene [71°].

Acetyl derivative. [222°]. Insol. in CS_2 (Beilstein a. Kurbatow, *A.* 196, 227; *B.* 11, 1979).

Di-chloro-nitro-aniline $C_6H_2Cl_2(NO_2)(NH_2)$ [3:4:6:1]. [175°]. Prepared by the action of alcoholic NH_3 on trichloronitrobenzene [58°] or, together with the (4,3,2,1)-isomeride [96°], by the nitration of acetyl-(4,3,1)-di-chloro-aniline. Yellow needles. Displacement of NH_2 by Cl gives tri-chloro-nitro-benzene [58°].

Acetyl derivative [124°]. Less sol. alcohol than the isomeride (1;4,5;6) (Beilstein a. Kurbatow, *A.* 196, 225; *B.* 11, 1978).

Di-chloro-nitro-aniline $C_6H_2Cl_2(NO_2)(NH_2)$ [2:6:4:1]. [188°]. Formed by chlorination of *p*-nitro-aniline (Körner, *G.* 4, 276; Witt, *B.* 8, 143). Lemon-yellow needles. Elimination of NH_2 gives di-chloro-nitro-benzene [65°].

Acetyl derivative $C_6H_2Cl_2(NO_2)(NHAc)$. [210°].

Di-chloro-di-nitro-aniline $C_6HCl_2(NO_2)_2(NH_2)$ [3:4:2:6:1]. [128°]. Formed by nitrating acetyl-(4,3,1)-di-chloro-aniline, and eliminating Ac by H_2SO_4 (Beilstein a. Kurbatow, *A.* 196, 235; *B.* 11, 1978). Large red needles.

Acetyl derivative $C_6HCl_2(NO_2)_2(NHAc)$ [246°].

Tri-chloro-*m*-nitro-aniline $C_6HCl_3(NO_2)(NH_2)$ [5:4:2:3:1]. [98°]. From *m*-nitraniline (1 pt.), conc. HCl (25 pts.) and water (20 pts.), by passage of a mixture of air and chlorine (Langer, *A.* 215, 110). Long, broad yellow needles (from light petroleum).

Tri-chloro-nitro-aniline $C_6HCl_3(NO_2)(NH_2)$ [2:4:5:6:1]. [124°]. Prepared by nitration of acetyl-tri-chloro-aniline [185°], and elimination of Ac by HCl. Yellow needles.

Acetyl derivative $C_6HCl_3(NO_2)(NHAc)$. [193°] (Beilstein a. Kurbatow, *A.* 196, 235; *B.* 11, 1980).

CHLORO-NITRO-ANISIDINE *v. Methyl ether* of CHLORO-NITRO-AMIDO-PHENOL.

CHLORO-NITRO-ANISOL *v. Methyl ether* of CHLORO-NITRO-PHENOL.

***o*-CHLORO-NITRO-BENZENE** $C_6H_4Cl(NO_2)$ [1:2]. **Mol. w. 157½.** [32·5°]. (243°). S.G. $\frac{2}{4}$ 1·368.

Formation.—**1.** Together with the *p*-isomeride, by nitrating chloro-benzene (Jungfleisch, *A. Ch.* [4] 15, 186; Laubenheimer, *B.* 7, 1765; 8, 1621; Sokoloff, *Z.* 1866, 621; Lesimple, *Z.* [2] 4, 225). 2. From chloro-nitro-aniline [157°] by elimination of NH_2 through the diazo-reaction (Beilstein a. Kurbatoff, *B.* 9, 633; *A.* 182, 107).—3. In small quantity by the action of PCl_5 on *o*-nitro-phenol (Engelhardt a. Latschinoff, *Z.* [2] 6, 225).

Properties.—Needles; converted by aqueous NaOH at 130° into *o*-nitro-phenol. Not attacked by alcoholic KCy.

***m*-Chloro-nitro-benzene** $C_6H_4Cl(NO_2)$ [1:3]. [45°]. (236° cor.).

Formation.—**1.** By chlorination of nitro-benzene in presence of iodine (Laubenheimer, *B.* 7, 1765) or $SbCl_3$ (Beilstein a. Kurbatoff, *A.* 182, 102).—2. From *m*-nitro-aniline by displacement of NH_2 by Cl through the diazo- reaction (Griess, *Pr.* 13, 381).

Preparation.—1. From nitro-benzene (500 g.) and Fe_2Cl_6 (10 g.) by chlorination (Varnholt, *J. pr.* [2] 36, 25).—2. By running a solution of $NaNO_2$ into a hot solution of *m*-nitro-aniline and Cu_2Cl_2 in dilute HCl (Sandmeyer, *B.* 17, 2650).

Properties. — Trimetric crystals; *a*:*b*:*c* = ·561:1:·498. Sublimes in flat needles. V. sol. ether, benzene, chloroform, CS_2, HOAc, and hot alcohol.

Reactions.—1. *Nitration* forms $C_6H_3Cl(NO_2)_2$ [89°].—2. Alcoholic KOH gives $(C_6H_4Cl)_2N_2O$. [97°].—3. Alcoholic KCy gives *o*-chloro-benzonitrile (Richter, *B.* 8, 1418).

***p*-Chloro-nitro-benzene** $C_6H_4Cl(NO_2)$ **[1:4].** [83°]. (242°). S.G. ^{22} 1·38.

Formation.—1. Together with the *o*-isomeride, by nitration of chloro-benzene (Riche, *A.* 121, 357; Jungfleisch, *A. Ch.* [4] 15, 186).—2. From *p*-nitro-aniline by displacement of NH_2 by Cl (Griess, *Pr.* 13, 381).—3. From *p*-nitro-phenol and PCl_5 (Engelhardt a. Latschinoff, *Z.* 1870, 230).—4. From (3,6,1)-chloro-nitro-aniline by elimination of NH_2 (Beilstein a. Kurbatoff, *A.* 182, 105).

Properties.—Trimetric plates.

Reactions.—1. Heating with aqueous Na_2CO_3 and NaOH at 130° slowly forms *p*-nitro-phenol. 2. Alcoholic KOH gives $(C_6H_4Cl)_2N_2O$ and, at 180°, $C_6H_4Cl.N_2.C_6H_4Cl$. If the alcohol be dilute $C_6H_4Cl.OEt$ is formed.—3. Alcoholic KCy gives *m*-chloro-benzonitrile.

Chloro-di-nitro-benzene $C_6H_3Cl(NO_2)_2$ [1:3:4?]. Mol. w. 202½. According to Laubenheimer (*B.* 9, 760, 768) the chloro-di-nitro-benzene formed by nitrating *m*-chloro-benzene, exists in four modifications, viz.:

(*α*). [36°]. Thick monoclinic prisms: *a*:*b*:*c* = 1·887:1:·981; *β* = 114° 14′. Gradually passes into the (*γ*) modification.

(*β*). [37°]. Monoclinic prisms, *a*:*b*:*c* = ·625:1:·560; *β* = 91° 27′. Gradually passes into the (*γ*) modification.

(*γ*). [39°]. Thin trimetric needles.

(*δ*). Liquid.

Reactions.—1. Aqueous NaOH forms chloro-nitro-phenol [39°].—2. *Aniline* forms $C_6H_3Cl(NO_2)(NPhH)$.—3. *Tin* and HCl reduce it to chloro-phenylene-diamine [72°].—4. Boiled with a solution of sodium sulphite it gives chloro-nitro-benzene-sulphonic acid and $NaNO_2$ (Laubenheimer, *B.* 15, 597).—5. *Phenyl-hydrazine* forms $C_6H_3Cl(NO_2).N_2H_2Ph$ [140°] (Willgerodt, *J. pr.* [2] 37, 355).

Chloro-di-nitro-benzene $C_6H_3Cl(NO_2)_2$ **[1:2:4].** [53·5°]. (315°). S.G. ^{12} 1·697.

Formation.—1. By nitration of *o*- or *p*-chloro-nitro-benzene (Jungfleisch, *A. Ch.* [4] 15, 186).—2. From di-nitro-phenol and PCl_5 (Clemm, *Z.* 1870, 274).

Properties.—Trimetric crystals; v. sl. sol. cold alcohol, v. sol. boiling alcohol and ether. Jungfleisch describes a physical isomeride [42°].

Reactions.—1. *Tin* and HCl form chloro-nitro-aniline [89°].—2. Strong aqueous KOH forms di-nitro-phenol.—3. Alcoholic NH_3 at 110° forms di-nitro-aniline [175°].—4. Alcoholic NMe_3 forms $C_6H_3(NO_2)_2(NMe_2)$ [78°].—5. *Di-methyl-aniline* gives $C_6H_3(NO_2)_2(NPhMe)$ [167°] (Leymann, *B.* 15, 1233).—6. By the action of KOH dissolved in an alcohol, it gives the ether of the di-nitro-phenol corresponding to the alcohol used (Willgerodt, *B.* 12, 762).—7. *Phenyl-hydrazine* in the cold forms $C_6H_3(NO_2)_2.N_2H_2Ph$ [120°] crystallising in red plates and converted by boiling HOAc into $C_6H_3(NO)_2.N_2Ph$ [247°] (Willgerodt, *J. pr.* [2] 37, 347, 449).

Chloro-tri-nitro-benzene $C_6H_2Cl(NO_2)_3$. [1:2:4:6]. *Picryl chloride.* Mol. w. 247½. [83°]. From tri-nitro-phenol (picric acid) and PCl_5 (Pisani, *A.* 92, 326; Clemm, *J. pr.* [2] 1, 145; *Z.* [2] 6, 444). Amber-yellow monoclinic tables (from ether) or nearly colourless needles (from alcohol). V. sol. boiling alcohol, sl. sol. ether. Combines with benzene and other aromatic hydrocarbons (Liebermann a. Palm, *B.* 8, 378).

Reactions.—1. *Water* or aqueous Na_2CO_3 converts it into tri-nitro-phenol.—2. *Ammonia* forms tri-nitro-aniline.—3. Alcoholic KOH forms $C_6H_2(NO_2)_3OEt$.—4. *Ethyl-hydrazine* forms $C_6H_2(NO_2)_3N_2H_2Et$ [200°] (Fischer, *A.* 199, 299).—5. *Phenyl-hydrazine* forms $C_{12}H_7N_5O_4$ [225°] (238°) (Willgerodt, *J. pr.* [2] 37, 357).—6. Alcoholic *di-methyl-amine* gives rise to $C_6H_2(NO_2)_3NMe_2$ [114°] (Van Romburgh, *R. T. C.* 2, 105).

Di-chloro-nitro-benzene $C_6H_3Cl_2(NO_2)$ **[1:3:4].** [33°]. Formed by nitrating *m*-di-chloro-benzene (Körner, *G.* 4, 305; *J.* 1875, 323; Beilstein a. Kurbatoff, *A.* 182, 97). Long needles (from alcohol). Converted by alcoholic NH_3 at 210° into $C_6H_3Cl(NH_2)(NO_2)$ [1:3:4] [125°]. Aqueous Na_2CO_3 has no action even at 290°. Alcoholic NaOH readily forms $C_6H_3Cl(OEt)(NO_2)$.

Di-chloro-nitro-benzene $C_6H_3Cl_2(NO_2)$ **[1:2:4].** [43°]. From $C_6H_2Cl_2(NO_2)(NH_2)$ [1:2:4:3] and [6:2:4:3] by displacement of NH_2 by H (Beilstein a. Kurbatoff, *A.* 192, 235). Formed also by nitration of *o*-di-chloro-benzene (B. a. K., *A.* 176, 41). Long needles (from alcohol). Converted by alcoholic ammonia at 210° into $C_6H_3Cl(NH_2)(NO_2)$ [105°].

Di-chloro-nitro-benzene $C_6H_3Cl_2(NO_2)$ **[1:4:6].** [55°]. (266°). S.G. ^{22} 1·669.

Formation.—1. By passing chlorine into cold nitro-benzene (75 g.) containing Fe_2Cl_6 (11·5 g.) (B. a. K.; Page, *A.* 225, 208).—2. By nitration of *p*-di-chloro-benzene (Jungfleisch).—3. From $C_6H_3Cl(NO_2)(NH_2)$ [4:3:1] by the action of Cu_2Cl_2 upon the diazo- compound (Claus a. Stiebel, *B.* 20, 1381).

Properties.—Triclinic crystals (from CS_2). Volatile with steam. Alcoholic KOH converts it into $C_6H_3(OH)Cl(NO_2)$ [1:4:6] [86°], together with $(C_6H_3Cl_2)_2N_2O$ and di-chloro-aniline [50°] (Laubenheimer, *B.* 7, 1600). By alcoholic NH_3 at 200° it is converted into chloro-nitro-aniline [115°].

Di-chloro-nitro-benzene $C_6H_3Cl_2(NO_2)$ **[1:3:5].** [65°]. From the di-chloro-nitro-anilines $C_6H_2(NH_2)Cl_2(NO_2)$ [1:2:4:6] and [1:2:6:4] by eliminating NH_2 (Körner, *G.* 4, 376; Witt, *B.* 7, 1604; *B.* 8, 144). Long thin laminæ (from alcohol). Volatile with steam. Alcoholic NH_3 does not act upon it.

Di-chloro-di-nitro-benzene $C_6H_2Cl_2(NO_2)_2$. [103°]. Formed by nitrating *m*-di-chloro-benzene (Körner, *G.* 4, 305; *J.* 1875, 323). Yellowish prisms. Converted by aqueous KOH into a chloro-di-nitro-phenol.

Di-chloro-di-nitro-benzene $C_6H_2Cl_2(NO_2)_2$ [1:4:2:6]. [87°] (J.); [104°] (Engelhardt a. Latschinoff). (312°). S.G. ^{16} 1·710. Formed, together with the following, by nitrating *p*-di-chloro-benzene (Jungfleisch). Small monoclinic plates. Boiling aqueous Na_2CO_3 converts it into di-chloro-phenol [80°].

Di-chloro-di-nitro-benzene $C_6H_2Cl_2(NO_2)_2$ [1:4:2:3 or 5] [107°] (J.); [101°] (E. a. L.). (318°). S.G. ^{16} 1·695. Formed as above. Monoclinic needles. Boiling aqueous Na_2CO_3 converts it into chloro-di-nitro-phenol [70°]. Alcoholic NH_3 at 160° forms $C_6H_2Cl_2(NH_2)(NO_2)$ [66°] (Körner, *G.* 4, 350).

Tri-chloro-nitro-benzene $C_6H_2Cl_3(NO_2)$ [1:2:4:5]. [57°]. (288°). S.G. ^{22} 1·790. Formed by nitrating $C_6H_3Cl_3$ [1:2:4] (Lesimple, *Bl.* [2] 6, 161; *A.* 137, 123). Sulphur-yellow monoclinic prisms (from CS_2). Converted by NH_3 into $C_6H_2(NH_2)Cl_2(NO_2)$ [1:3:4:6].

Tri-chloro-nitro-benzene $C_6H_2Cl_3(NO_2)$ [1:2:3:4]. [56°]. From *c*-tri-chloro-benzene and fuming HNO_3 (Beilstein a. Kurbatow, *A.* 192, 235). Colourless silky needles (from alcohol). V. sol. ether and CS_2, m. sol. dilute (50 per cent.) acetic acid, sl. sol. alcohol. May be reduced to tri-chloro-aniline [68°]. Alcoholic NH_3 forms $C_6H_2Cl_2(NH_2)(NO_2)$ [1:2:3:4] [163°].

Tri-chloro-nitro-benzene $C_6H_2Cl_3(NO_2)$ [1 3:5:2]. [68°]. From *s*-tri-chloro-benzene and fuming HNO_3 (Beilstein a. Kurbatoff, *A.* 192, 233). Long needles (from alcohol). V. sol. CS_2 and light petroleum. Ammonia at 230° forms $C_6H_2(NH_2)_2Cl(NO_2)$ [1:3:5:2].

Tri-chloro-nitro-benzene $C_6H_2Cl_3(NO_2)$ [1:3:6:2]. [89°]. Formed from $C_6H_2Cl_2(NH_2)(NO_2)$ [3:6:1:2] by diazo-reaction (B. a. K.). Colourless needles (from light petroleum). V. sol. alcohol, less sol. light petroleum.

Tri-chloro-di-nitro-benzene $C_6HCl_3(NO_2)_2$. [103·5°]. (335°). S.G. ^{25} 1·85. Formed by nitration of *u*-tri-chloro-benzene (Jungfleisch). Light yellow six-sided prisms. Insol. cold alcohol, sol. hot alcohol and ether.

Tri-chloro-di-nitro-benzene $C_6HCl_3(NO_2)_2$. [1:3:5:2:4]. [130°]. Formed by nitrating *s*-tri-chloro-benzene (Jackson a. Wing, *Am.* 9, 353). Thick white prisms (from alcohol). Sol. cold alcohol and ether; v. sol. benzene, CS_2, and chloroform.

Tri-chloro-tri-nitro-benzene $C_6Cl_3(NO_2)_3$ [1:3:5:2:4:6]. [187°]. Formed by nitrating the preceding (Jackson a. Wing, *Am.* 9, 354). Thick white needles (from alcohol). V. sl. sol. water, sol. alcohol, v. sol. ether, benzene, and CS_2.

Tetra-chloro-nitro-benzene $C_6H(NO_2)Cl_4$ [1:2:3:4:6]. [22°]. From *u*-tetra-chloro-benzene and fuming HNO_3 (Beilstein a. Kurbatoff, *A.* 192, 238). Colourless needles. V. sol. benzene, CS_2, and hot alcohol.

Tetra-chloro-nitro-benzene $C_6HCl_4(NO_2)$ [1:2:3:4:5]. [64·5°]. From *c*-tetra-chloro-benzene and fuming HNO_3 (Beilstein a. Kurbatoff, *A.* 192, 239). Small needles, sl. sol. alcohol.

Tetra-chloro-nitro-benzene $C_6H(NO_2)Cl_4$ [1.2:3:5:6]. [99°]. (304°). S.G. ^{22} 1·744. From *s*-$C_6H_2Cl_4$ and fuming HNO_3. Some chloranil is also formed, but light petroleum dissolves the $C_6H(NO_2)Cl_4$ only (Beilstein a. Kurbatow, *A.* 192, 236; *cf.* Jungfleisch, *loc. cit.*). Formed also by passing chlorine at 100° into nitro-benzene containing Fe_2Cl_6 (Page, *A.* 225, 208). Needles (from alcohol).

Penta-chloro-nitro-benzene $C_6Cl_5(NO_2)$. [146°]. (328°). S.G. ^{25} 1·718. Formed by heating penta-chloro-benzene with fuming HNO_3 (Jungfleisch). Slender needles (from alcohol) or monoclinic tables (from CS_2). V. sol. boiling alcohol, CS_2, and chloroform.

CHLORO-NITRO-BENZENE-SULPHONIC ACID $C_6H_3(Cl)(NO_2)SO_3H$ [1:4:3]. Formed by boiling (1:3:4)-chloro-di-nitro-benzene with a solution of sodic sulphite.—NaA′ 2aq: glistening prisms or needles, sol. water and alcohol.

Amide [159°]. Plates or needles. Sol. alcohol, sl. sol. water (Laubenheimer, *B.* 15, 597).

***m*-Chlor-nitro-benzene sulphonic acid** $C_6H_3(Cl)(NO_2)(SO_3H)$ [1:3:*x*]. Prepared by sulphonation of *m*-chloro-nitro-benzene. On reduction it gives a chloro-amido-phenyl-mercaptan which does not form anhydro- compounds.

Salts.—$A'_2Ba^{\times}$: white sparingly soluble needles.—$A'_2Pb^{\times}$: soluble needles.—A′K: white soluble needles (Allert, *B.* 14, 1434).

(α)-Chloro-nitro-benzene-sulphonic acid $C_6H_3(Cl)(NO_2)SO_3H$ [1:3:?]. Formed together with an isomeric (β)-acid by sulphonation of *m*-chloro-nitro-benzene.

Salts.—A′K: needles or plates, sol. alcohol. A′Na 2½aq: yellow needles.—A'_2Ba 2aq: small brown needles or plates, v. sol. alcohol.—A'_2Sr ½aq: thick brown plates, sol. alcohol (Post a. Meyer, *B.* 14, 1606).

(β)-Chloro-nitro-benzene-sulphonic acid $C_6H_3(Cl)(NO_2)SO_3H$ [1:3:?]. Formed together with the preceding by sulphonation of *m*-chloro-nitro-benzene.

Salts.—A′K ½aq: light yellow prisms.—A'_2Ba ½aq: small yellow needles, insol. alcohol.—A'_2Sr: yellow crystalline powder (Post a. Meyer, *B.* 14, 1606).

***m*-Chloro-nitro-benzene di-sulphonic acid** $C_6H_2(Cl)(NO_2)(SO_3H)_2$ [1:3:?:?]. Prepared by sulphonating *m*-chloro-nitro-benzene with boiling H_2SO_4.—$A''K_2$: pearly scales (Allert, *B.* 14, 1436).

CHLORO-NITRO-BENZOIC ACID $C_6H_3Cl(NO_2)(CO_2H)$ [2:4:1]. [137°]. Formed by oxidising chloro-nitro-toluene [65°] by alkaline $KMnO_4$ (Wachendorff, *A.* 185, 275; Lellmann, *B.* 17, 534).

Chloro-nitro-benzoic acid $C_6H_3Cl(NO_2)(CO_2H)$ [3:2:1]. [137°]. Formed by the action of H_2SO_4 and HNO_3 on the di-chloro-benzoic acid [156°] obtained by direct chlorination of benzoic acid (Claus a. Bücher, *B.* 20, 1624). Either this or the following acid ought to be identical with the isomeride [235°].

Chloro-nitro-benzoic acid $C_6H_3Cl(NO_2)(CO_2H)$ [3:4:1]. [136°]. Obtained by the action of H_2SO_4 and HNO_3 on the di-chloro-benzoic acid [201°] formed by chlorination of benzoic acid (C. a. B.).— BaA'_2 4aq (B. a. K.).

(β)-Chloro-nitro-benzoic acid $C_6H_3Cl(NO_2)(CO_2H)$ [3:6:1]. [138°]. One of the products of the nitration of *m*-chloro-benzoic acid (Ulrich, *A.* 222, 97).

Salts.—BaA'_2.—CaA'_2aq.—PbA'_2.—KA' 2½aq.

Ethyl ether EtA'. [282°] (Cunze a. Hübner, *A.* 135, 113).

Anilide $C_6H_3Cl(NO_2)(CONPhH)$: [164°]; needles.

Chloro-nitro-benzoic acid $C_6H_3Cl(NO_2)CO_2H$ [4:2:1]. [139°]. From $C_6H_3Cl(NO_2)Me$ [4:2:1] by oxidation with HNO_3 (S.G. 1·1) (Varnholt, *J. pr.* [2] 36, 30). Formed also by saponifying its nitrile with dilute H_2SO_4. Long needles; sl. sol. cold water and CS_2, m. sol. chloroform.

Nitrile $C_6H_3Cl(NO_2)CN$. [98°]. From the corresponding chloro-nitro-aniline by Sandmeyer's reaction (Claus, *J. pr.* [2] 37, 197). Needles, v. sol. ether and alcohol, m. sol. cold water.

Chloro-nitro-benzoic acid $C_6H_3Cl(NO_2)CO_2H$ [1:3:5]. [147°]. From $C_6H_3(NH_2)(NO_2)CO_2H$, conc. HCl, and nitrous acid gas (Hübner, *A.* 222, 89). Small needles. V. sol. alcohol, ether and glacial acetic acid.

Salts.—BaA'_2 4aq.—PbA'_2.

Chloro-nitro-benzoic acid $C_6H_3Cl(NO_2)CO_2H$ [2:5:1]. [164°]. S. ·361 at 15°. Formed by nitration of *o*-chloro-benzoic acid (Wilkens a. Rack, *A.* 222, 195; *cf.* Kekulé, *A.* 117, 153). Formed also by the action of PCl_5 on nitro-*o*-oxy-benzoic acid (Hübner, *Z.* [2] 2, 614). Long thin monoclinic needles (from dilute HCl). V. sol. hot water, sl. sol. cold water, v. e. sol. alcohol, ether and benzene.

Salts. — NH_4A'. — NaA'. — BaA'_2 3aq. — SrA'_2 4½aq.—CaA'_2 2aq.—ZnA'_2 5½aq.—CdA'_2 5aq. —PbA'_2.

Ethyl ether EtA'. [29°].

Nitrile $C_6H_3Cl(NO_2)CN$. [106°]. Formed by nitrating the nitrile of *o*-chloro-benzoic acid (Henry, *B.* 2, 493).

Chloro-nitro-benzoic acid $C_6H_3Cl(NO_2)CO_2H$ [4:3:1]. [180°]. Formed by nitration of *p*-chloro-benzoic acid (Reveill, *A.* 222, 182). Formed also by oxidising the corresponding chloro-nitro-toluene (Hubner, *Z.* [2] 2, 614).

Salts.—$BaA'_2$4aq.—CaA'_2 5½aq.—MgA'_2 5aq.

Ethyl ether EtA'. [59°].

Anilide $C_6H_3Cl(NO_2)CO.NPhH$. [131°].

Nitrile $C_6H_3Cl(NO_2)CN$. [101°]. From the corresponding chloro-nitro-aniline by Sandmeyer's reaction with cuprous cyanide (Claus, *J. pr.* [2] 37, 197). Needles, sl. sol. cold water.

Chloro-nitro-benzoic acid $C_6H_3Cl(NO_2)CO_2H$ [3:4:1]. [186°]. From the nitrile by saponification with dilute H_2SO_4 (Claus, *J. pr.* [2] 37, 200). White needles. V. sol. hot water, alcohol, ether, chloroform, sl. sol. cold water, CS_2.—**Salts.**—BaA'_2 2aq. — CaA'_2 2aq. — AgA': needles (from water).

Nitrile $C_6H_3Cl(NO_2)CN$. [87°]. From the corresponding chloro-nitro-aniline by displacement of NH_2 by Cy. Colourless needles, sl. sol. cold, v. sol. hot, water.

(a)-Chloro-nitro-benzoic acid $C_6H_3Cl(NO_2)(CO_2H)$ [3:2:1]. [235°]. From *m*-chloro-benzoic acid and fuming HNO_3. Separated by water from the more soluble (*β*)-isomeride [137°] (Ulrich, *A.* 222, 95). Long thin needles, or six-sided tables. V. sl. sol. water, v. sol. ether.

Salts.—BaA'_2 4aq.—CaA'_2 3aq.

Anilide $C_5H_3Cl(NO_2)(CONPhH)$. [186°].

Chloro-di-nitro-benzoic acid $C_6H_2Cl(NO_2)_2CO_2H$ [2:(3 or)5:3?:1]. [238°]. By nitration of *o*-chloro-benzoic acid (Wilkens a. Rack, *A.* 222, 201). Small colourless needles (from petroleum). V. sol. water, alcohol, ether, or petroleum, sl. sol. benzene.

Di-chloro-nitro-benzoic acid $C_6H_2Cl_2(NO_2)(CO_2H)$ [4:3:*x*:1]. [160°]. Obtained by nitration of (4,3,1)-di-chloro-benzoic acid [201°], which is formed by direct chlorination of benzoic acid (Claus a. Bücher, *B.* 20, 1621). Small needles. Sol. water.

Di-chloro-nitro-benzoic acid $C_6H_2Cl_2(NO_2)(CO_2H)$ [3:2:*x*:1]. [215°]. Prepared by nitrating (3,2,1)-di-chloro-benzoic acid [156°], which is got by chlorinating benzoic acid (Claus a. Bücher, *B.* 20, 1621). Sl. sol. boiling water.—BaA'_2 4aq: lens-shaped aggregates of small needles.

Tri-chloro-nitro-benzoic acid $C_6HCl_3(NO_2)(CO_2H)$ [2:4:6:3:1]. [220°]. From $C_6HCl_3(CO_2H)$ [2:4:6:1] by nitration (Beilstein a. Kuhlberg, *A.* 152, 239). Small needles (from water). V. sl. sol. boiling water.—CaA'_2 1½aq.—BaA'_2 2aq: crystalline powder.

Tetra-chloro-nitro-benzoic acid $C_6Cl_4(NO_2)CO_2H$ [5:4:3:2:6:1]. Formed by nitration of tetra-chloro-benzoic acid [5:4:3:2:1], by a mixture of fuming HNO_3 and conc. H_2SO_4. Silvery plates. Sol. water. By tin and HCl it is reduced to tetra-chloro-amido-benzoic acid.

Salts.—A'_2Ba 2½aq: v. sol. water, small colourless needles.—A'_2Ca: easily soluble glistening plates (Tust, *B.* 20, 2411).

CHLORO-NITRO-BENZOIC ALDEHYDE $C_6H_3Cl(NO_2)CHO$ [3:4:1]. [62°]. From [3,4,1]-chloro-nitro-toluene by chlorinating and treating the resulting $C_6H_3Cl(NO_2).CH_2Cl$ with lead or copper nitrate solution (Landsberg, *D. P. J.* 262, 139). White needles (from water).

Di-chloro-*o*-nitro-benzoic aldehyde $C_6H_2Cl_2(NO_2)CHO$. [138°]. Obtained by nitration of di-chloro-benzoic aldehyde with a mixture of HNO_3 and H_2SO_4 (Gnehm, *B.* 17, 753). Pearly plates or needles. By treatment with acetone and NaOH it yields tetra-chloro-indigo.

CHLORO-NITRO-CAMPHOR *v.* Camphor.

α-CHLORO-*p*-NITRO-CINNAMIC ACID $C_6H_4(NO_2).CH:CCl.CO_2H$. [224°]. From *α*-chloro-*p*-nitro-*β*-oxy-*β*-phenyl-propionic acid and HCl (S.G. 1·1) at 180° (Lipp, *B.* 19, 2646). Prisms (from alcohol).

CHLORO-DI-NITRO-CYMENE $C_6HCl(NO_2)_2(CH_3)(C_3H_7)$ [2:?:?:1:4]. [109°]. Monoclinic prisms. Prepared by nitration of chloro-cymene [214°] (Gerichten, *B.* 11, 1091).

Chloro-di-nitro-cymene $C_6HCl(NO_2)_2(CH_3)(C_3H_7)$ [3:?:?:1:4]. [101°]. From di-nitro-thymol and PCl_5 (Ladenburg a. Engelbrecht, *B.* 10, 1220). Light yellow prisms.

ω-Di-chloro-nitro-cymene $C_6H_3(CHCl_2)(NO_2)(C_3H_7)$ [1:3:4]. From nitro-cuminic aldehyde $C_6H_3(CHO)(NO_2)(C_3H_7)$ and PCl_5 (Widmann, *B.* 15, 167). Oil.

CHLORO-DI-NITRO-ETHANE $C_2H_3Cl(NO_2)_2$? A liquid formed when ethylidene chloride is heated in a sealed tube with HNO_3 at 100° (Lauterbach, *B.* 12, 677).

Tetra-chloro-di-nitro-ethane $C_2Cl_4N_2O_4$. Formed by direct union of tetra-chloro-ethylene with nitric peroxide (Hoch a. Kolbe, *J. pr.* [2] 4, 60). Feathery needles (from alcohol); insol. water. Volatile with steam. Decomposes at 140°. Alcoholic KOH forms long prisms of $C_2Cl_3(NO_2)_2(OK)$.

CHLORO-NITRO-ETHYL-ANILINE $C_8H_9ClN_2O_2$ *i.e.* $C_6H_3Cl(NO_2).NHEt$ [5:2:1]. [84°]. From chloro-di-nitro-benzene and an alcoholic solution of ethyl-aniline (Laubenheimer, *B.* 11, 1156). Golden needles; sl. sol. cold alcohol.

DI-CHLORO-NITRO-ETHYL-BENZENE $C_6H_5.CHCl.CHCl.NO_2$. [30°]? Formed by the union of Cl with $C_6H_5CH:CH.NO_2$ (Priebs, *A.* 225, 344). Usually an oil. Volatile with steam. Aqueous NaOH forms $C_6H_5.CCl:CH.NO_2$.

Di-chloro-nitro-ethyl-benzene $C_6H_2Cl_2(NO_2)Et$ [1:4:*x*:2]. [175°]. Formed by boiling di-chloro-ethyl-benzene with HNO_3 and H_2SO_4 for 50 hours (Istrati, *Bl.* [2] 48, 41). Crystalline plates, sol. hot water. Gives a yellowish-white pp. with Fe_2Cl_6.

Di-chloro-tri-nitro-ethyl-benzene $C_6Cl_2(NO_2)_3Et$. [195°]. Formed at the same time as the preceding (Istrati). Groups of small crystals; insol. water, v. sol. alcohol. Fe_2Cl_6 pps. its alcoholic solution.

Tetra-chloro-nitro-ethyl-benzene $C_6Cl_4(NO_2)(C_2H_5)$ [1:3:4:5:2:6]. [30°]. Formed by passing C_2H_4 into a mixture of Al_2Cl_6 and $C_6HCl_4(NO_2)$ (Istrati, *A. Ch.* [6] 6, 498). Gelatinous solid, v. sol. ether and $CHCl_3$. Decomposes on distillation, giving tetra-chloro-di-ethyl-benzene.

TRI-CHLORO-NITRO-ETHYLENE $C_2Cl_3NO_2$(?) Formed by adding C_2Cl_4 to a cooled mixture of H_2SO_4 and fuming HNO_3 (Hoch, *J. pr.* [2] 6, 95). Pungent yellow oil; decomposed by water and alkalis. Br at 150° converts it into $C_2Cl_3Br_2(NO_2)$ [c. 120°]. Liquid nitric peroxide at 115° forms feathery crystals of an unstable compound $C_2Cl_3(NO_2)_3$.

CHLORO-NITRO-MESITYLENE $C_9H_{10}ClNO_2$ *i.e.* $C_6HCl(NO_2)Me_3$ [2:4:1:3:5]. [57°]. Formed by nitrating chloro-mesitylene (Fittig a. Hoogewerff, *A.* 150, 324; *Z.* [2] 5, 168). Pale yellow spicular crystals, v. sol. alcohol.

Chloro-di-nitro-mesitylene $C_6Cl(NO_2)_2Me_3$. [179°]. The chief product of the action of fuming HNO_3 on chloro-mesitylene (F. a. H.). Long colourless needles (from alcohol). Sl. sol. cold alcohol. May be sublimed.

CHLORO-NITRO-METHANE $CH_2Cl(NO_2)$. (123°). S.G. ^{15} 1·466. Formed by the action of chlorine-water on sodium nitro-methane: $CH_2Na(NO_2) + Cl_2 = NaCl + CH_2Cl(NO_2)$. The presence of Cl and the chlorous nitroxyl (NO_2) render the hydrogen displaceable by sodium: hence the liquid dissolves in alkali.

Chloro-di-nitro-methane $CClH(NO_2)_2$.

Potassium salt $CKCl(NO_2)_2$: large yellow crystals, sol. water, explodes at 145° (Losanitsch, *B.* 17, 849).

Di-chloro-di-nitro-methane $CCl_2(NO_2)_2$. (above 100°). S.G. ^{15} 1·685 (M.). Formed by passing chlorine into an aqueous solution of $CKCl(NO_2)_2$ (Losanitsch, *B.* 17, 848).

Preparation.—Crude naphthalene tetrachloride (200 grms.) is treated with fuming HNO_3 (400 c.c.) in a large retort; when the reaction is over, the mixture is distilled as long as the residue in the retort froths strongly. The distillate is diluted with twice its bulk of water and the di-chloro-di-nitro-methane distilled off with steam; the yield is 4 p.c. of the naphthalene tetrachloride (Marignac, *A.* 88, 16; Raschig, *B.* 18, 3326).

Properties.—Pungent oil: volatile with steam. On reduction with $SnCl_2$ it yields hydroxylamine.

Tri-chloro-nitro-methane $CCl_3(NO_2)$. *Chloropicrin. Nitro-chloroform.* Mol. w. 164½. (112° cor.). S.G. $\frac{0}{4}$ 1·6923 (Thorpe). C.E. (0°–10°) ·001106; (0°–100°) ·0012256. S. (alcohol of 80·5 p.c.) ·743 (Cossa, *G.* 2, 181). S.V. 110·49. μ_D 1·4679 (Gladstone, *C. J.* 23, 101).

Formation.—1. By distilling picric acid and other nitro- compounds with bleaching-powder (Stenhouse, *A.* 66, 241; *P. M.* [3] 33, 53; Gerhardt a. Cahours, *Compt. chim.* 1849, 34, 170).—2. By distilling chloral with conc. HNO_3 (Kekulé, *A.* 106, 144).—3. From chloroform and HNO_3 (Mills, *C. J.* 24, 641).—4. By distilling alcohol with sodic chloride, KNO_3 and H_2SO_4 (Kekulé, *A.* 101, 212).

Preparation.—A saturated (at 30°) solution of picric acid (1 pt.) is mixed with bleaching powder (10 pts.) previously made into paste with water, and the mixture distilled (Hofmann, *A.* 139, 111).

Properties.—Pungent liquid. V. sl. sol. water, v. sol. alcohol and ether.

Reactions.—1. May be *reduced* by iron and acetic acid to methylamine (Geisse, *A.* 109, 282). 2. Fuming HI at 100° forms NH_3, HCl, and CO_2 (Mills, *C. J.* 17, 153).—3. NaOEt in absolute alcohol gives orthocarbonic ether $C(OEt)_4$ (Bassett, *C. J.* 17, 198).—4. KCy and dilute alcohol forms chloro-nitro-malonitrile $C(NO_2)ClCy_2$, an unstable compound which gives with aqueous lead acetate a pp. $C(NO_2)ClCy_23PbO$ and with silver nitrate $(C(NO_2)ClCy_2)_3(AgNO_3)_48aq$ (Bassett, *C. J.* 19, 352).—5. Alcoholic *ammonia* forms guanidine $C(NH)(NH_2)_2$ (Hofmann, *C. J.* 19, 249).—6. Alcoholic KOH gives KCl and KNO_2 (S.).—7. Alcoholic KOAc at 100° gives KCl, K_2CO_3, and KNO_2 (Bassett, *C. J.* 18, 31).—8. K_2SO_3 forms $CH(NO_2)(SO_3K)_2$ (Rathke, *A.* 161, 149).—9. With benzene in presence of Al_2Cl_6 it yields tri-phenyl-carbinol and tri-phenyl-methane (Elbs, *B.* 16, 1274).—10. With phenol and Al_2Cl_6 the chief product is aurin (tri-oxy-tri-phenyl-carbinol) (E.).—11. With naphthalene and Al_2Cl_6 it yields tri-naphthyl-carbinol (E.).

DI-CHLORO-NITRO-TETRA-METHYL-DI-AMIDO-TRI-PHENYL-METHANE $C_{23}H_{23}N_3Cl_2O_2$ *i.e.* $C_6H_4(NO_2).CH(C_6H_3Cl.NMe_2)_2$. [208°]. From *m*-chloro-di-methyl-aniline, *p*-nitro-benzoic aldehyde, $ZnCl_2$, and HCl (Kock, *B.* 20, 1562). Lemon-yellow scales (from benzene). May be reduced to $C_{23}H_{25}N_3Cl_2$ [181°].

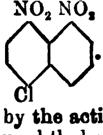
Picrate $C_{35}H_{29}N_9O_{16}Cl_2$. [189°].

CHLORO-NITRO-DI-METHYL-ANILINE $C_6H_3Cl(NO_2)(NMe_2)$ [4:3:1]. [56°]. Formed together with other products by the action of nitrous acid upon *p*-chloro-di-methyl aniline (Koch, *B.* 20, 2459; *cf.* Heidlberg, *B.* 20, 149).

CHLORO-NITRO-NAPHTHALENE $C_{10}H_6Cl(NO_2)$ [1:4]. [85°]. From (α)-chloro-naphthalene and cold HNO_3 (S.G. 1·4). Extremely slender, light yellow concentric needles. PCl_5 gives ('β')-di-chloro naphthalene. Tin and HCl reduce it to (α)-naphthylamine (Atterberg, *B.* 9, 927).

('α')-Chloro-di-nitro-naphthalene $C_{10}H_5Cl(NO_2)_2$ [1:4:1′]. [106°]. Formed, together with the foregoing by treating (α)-chloro-naphthalene with warm HNO_3 (S.G. 1·4) (A.; Faust a. Saame, *A.* 160, 68). Long yellow pliable needles, v. sol. hot alcohol. PCl_5 converts it into (δ)-tri-chloro-naphthalene.

('β')-Chloro-di-nitro-naphthalene probably



. [180°] (A.); [175°] (E.). Obtained by the action of hot fuming HNO_3 on (α)-chloro-naphthalene (Atterberg). Formed by the action of HNO_3 upon chloro-nitro-(α)-naphthoic acid [225°] (Ekstrand, *B.* 18, 2881). Glistening yellow needles (from alcohol). Sl. sol. boiling alcohol.

('β')-Di-chloro-nitro-naphthalene $C_{10}H_5Cl_2(NO_2)$ [1:4:1′]. [92°]. From ('β')-di-chloro-naphthalene and HNO_3 (S.G. 1·45) (Widmann, *Bl.* [2] 28, 509). With PCl_5 it gives (δ)-tri-chloro-naphthalene.

Di-chloro-nitro-naphthalene $C_{10}H_5Cl_2(NO_2)$. [95° ?]. Formed, together with an isomeride [142°], by the action of cold conc. HNO_3 on (δ)-di-chloro-naphthalene (Alén, *Bl.* [2] 36, 433).

Di-chloro-nitro-naphthalene $C_{10}H_5Cl_2(NO_2)$. [c. 114°]. From (ε)-di-chloro-naphthalene and cold fuming HNO_3 (Alén, *Bl.* [2] 36, 435). Yellowish needles.

(η)-Di-chloro-nitro-naphthalene $C_{10}H_5Cl_2(NO_2)$. [119°]. Formed by adding fuming HNO_3 to a solution of (γ)-di-chloro-naphthalene in HOAc (Clève, *Bl.* [2] 29, 499). Golden-yellow needles; m. sol. boiling alcohol. PCl_5 forms (ε)-tri-chloro-naphthalene.

Di-chloro-nitro-naphthalene $C_{10}H_5Cl_2(NO_2)$. [139°]. Formed, together with the isomeride [114°], by treating (ε)-di-chloro-naphthalene with cold fuming HNO_3 (Alén, *Bl.* [2] 36, 435). Needles, turning brownish-violet in the air.

Di-chloro-nitro-naphthalene $C_{10}H_5Cl_2(NO_2)$. [142°]. From (δ)-di-chloro-naphthalene and cold conc. HNO_3 (Alén, *Bl.* [2] 36, 433). Needles, turning green in the air.

(γ)-Di-chloro-nitro-naphthalene $C_{10}H_5Cl_2(NO_2)$. [142°]. From (γ)-di-chloro-naphthalene and cold HNO_3 (S.G. 1·4) (Atterberg, *B.* 9, 928). Short sulphur-yellow brittle prisms (from HOAc). PCl_5 gives (δ)-tri-chloro-naphthalene.

('β')-Di-chloro-di-nitro-naphthalene $C_{10}H_4Cl_2(NO_2)_2$. [158°]. Formed by adding HNO_3 (S.G. 1·48) to a solution of ('β')-di-chloro-naphthalene in HOAc (Widmann, *Bl.* [2] 28, 510). Long yellow needles: sl. sol. alcohol.

(γ)-Di-chloro-di-nitro-naphthalene $C_{10}H_4Cl_2(NO_2)_2$. [246°]. From (γ)-di-chloro-nitro-naphthalene [142°] and HNO_3 mixed with H_2SO_4 (Atterberg, *B.* 9, 1780). Light yellow brittle prismatic needles; v. sl. sol. all solvents. PCl_5 gives (ε)-tetra-chloro-naphthalene.

(δ)-Di-chloro-di-nitro-naphthalene $C_{10}H_4Cl_2(NO_2)_2$. [246°]. Formed by adding fuming HNO_3 to a solution of (δ)-di-chloro-naphthalene in HOAc (Alén, *Bl.* [2] 36, 434). Pale yellow prisms, turning green in air.

(ε)-Di-chloro-di-nitro-naphthalene $C_{10}H_4Cl_2(NO_2)_2$. [253°]. Formed by acting on (ε)-di-chloro-naphthalene dissolved in glacial acetic acid with fuming HNO_3 (Alén, *Bl.* [2] 36, 435; Claus a. Dehne, *B.* 15, 320). Pale yellow needles, turning red in air. PCl_5 gives (ζ)-tri-chloro-naphthalene. Alcoholic KOH forms $C_{10}H_4(OEt)_2(NO_2)_2$.

Di-chloro-tri-nitro-naphthalene $C_{10}H_3Cl_2(NO_2)_3$. [178°]. From ('α')-di-chloro-naphthalene, H_2SO_4, and HNO_3 (S.G. 1·48) (Widmann, *Bl.* [2] 28, 505). Brittle yellow prisms (from HOAc); sl. sol. alcohol, v. sol. chloroform.

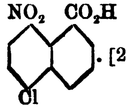
(ε)-Di-chloro-tri-nitro-naphthalene $C_{10}H_3Cl_2(NO_2)_3$. [200°]. Formed by boiling (ε)-di-chloro-naphthalene with fuming HNO_3 (Alén, *Bl.* [2] 36, 435). Pale yellow needles. PCl_5 gives (η)-tetra-chloro-naphthalene [160°].

Di-chloro-tri-nitro-naphthalene $C_{10}H_3Cl_2(NO_2)_3$. [201°]. Formed by acting on (δ)-di-chloro-naphthalene with fuming HNO_3 at 100° (Alén, *Bl.* [2] 36, 434). Pale yellow needles, turning greenish in the air.

Tetra-chloro-nitro-naphthalene $C_{10}H_3Cl_4(NO_2)$. [155°]. From (δ)-tetra-chloro-naphthalene and conc. HNO_3 (Atterberg a. Widmann, *B.* 10, 1841). Large pale-yellow trimetric prisms (from alcohol-toluene). PCl_5 gives ('β')-penta-chloro-naphthalene.

CHLORO-NITRO-(α)-NAPHTHOIC ACID

$C_{10}H_5Cl(NO_2)(CO_2H)$ probably



. [225°].

Formed by nitration of chloro-(α)-naphthoic acid [245°]. Prismatic needles.

Ethyl ether A′Et: [121°]; tables (from alcohol) (Ekstrand, *B.* 18, 2881).

TRI-CHLORO-TETRA-NITRO-DI-(β)-NAPHTHYL-ETHANE $C_{22}H_{11}(NO_2)_4Cl_3$. [258°]. From tri-chloro-di-(β)-naphthyl-ethane $(C_{10}H_7)_2CH.CCl_3$ and HNO_3 (Grabowski, *B.* 11, 298). Crystalline powder, insol. alcohol, ether, and HOAc.

DI-CHLORO-TETRA-NITRO-DI-(α)-NAPHTHYL-ETHYLENE $C_{22}H_{10}(NO_2)_4Cl_2$. [214°]. From di-chloro-di-(α)-naphthyl-ethylene $(C_{10}H_7)_2C{:}CCl_2$ and fuming HNO_3 (Grabowski, *B.* 11, 299).

Di-chloro-tetra-nitro-di-(β)-naphthyl-ethylene $C_{22}H_{10}(NO_2)_4Cl_2$. [293°]. Formed by nitrating di-chloro-di-(β)-naphthyl-ethylene (G.).

CHLORO-NITRO-*o*-OXY-BENZOIC ACID $C_6H_2(Cl)(NO_2)(OH)CO_2H$ [5:?:2:1]. [163°]. Prepared by nitration of *m*-chloro-salicylic acid (Smith a. Peirce, *B.* 13, 34; *Am.* 1, 176). Short needles.

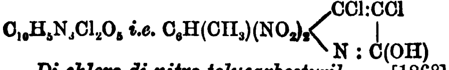
Salts.—A′K: soluble yellow needles.—A'_2Ba: sparingly soluble orange needles.—A′Ag: insol. pp.

Ethyl ether A′Et: [89°]; colourless flat needles.

Amide [199°]. Sl. sol. water, v. sol. alcohol.

Chloro-di-nitro-*o*-oxy-benzoic acid $C_6HCl(NO_2)_2(OH).CO_2H$. [78°]. From chloro-salicylic acid and fuming HNO_3 (Hasse, *B.* 10, 2191). Long yellow needles (from water).

(*Py.* 1:2)-**DI-CHLORO**-(*B.* 1:3or4)-**DI-NITRO**-(*Py.* 3)-**OXY**-(*B.* 2)-**METHYL-QUINOLINE**



$C_{10}H_5N_3Cl_2O_5$ *i.e.* $C_6H(CH_3)(NO_2)_2\left\langle\begin{array}{l} CCl{:}CCl \\ \qquad | \\ N : C(OH) \end{array}\right.$

Di-chloro-di-nitro-tolucarbostyril. [186°]. Formed by nitration of (*Py.* 1:2:3)-di-chloro-oxy-(*B.* 2)-methyl-quinoline in cold H_2SO_4 solution by means of N_2O_3. Long yellow needles with greenish reflex (Rügheimer a. Hoffmann, *B.* 18, 2982).

β-CHLORO-*o*-NITRO-*a*-OXY-β-PHENYL-PROPIONIC ACID $C_9H_8ClNO_5$ *i.e.* $[2:1]C_6H_4(NO_2).CHCl.CH(OH).CO_2H$. [126°]. From *o*-nitro-*a*-oxy-cinnamic acid and fuming HCl (Lipp, *B.* 19, 2649). Needles (from ether-ligroïn). Alcoholic KOH re-converts it into *o*-nitro-*a*-oxy-cinnamic acid.

β-Chloro-*p*-nitro-*a*-oxy-β-phenyl-propionic acid $[4:1]C_6H_4(NO_2).CHCl.CH(OH).CO_2H$. [168°]. From *p*-nitro-*a*-oxy-cinnamic acid and fuming HCl (L.). Small glittering needles; sl. sol. cold water. The Ba salt is split up by boiling water into CO_2, $BaCl_2$, and *p*-nitro-phenyl-acetic aldehyde. Alcoholic KOH gives *p*-nitro-*a*-oxy-cinnamic acid.

a-Chloro-*o*-nitro-β-oxy-β-phenyl-propionic acid $[2:1]C_6H_4(NO_2).CH(OH).CHCl.CO_2H$. [120°]. Formed by passing chlorine into a solution of *o*-nitro-cinnamic acid in dilute aqueous NaOH (Baeyer, *B.* 13, 2261). Crystalline mass (from benzene-ligroïn). Sol. ether. Converted by NaOH and $FeSO_4$ into indole. Alcoholic KOH gives *o*-nitro-β-oxy-cinnamic acid.

a-Chloro-*p*-nitro-β-oxy-phenyl-propionic acid $[4:1]C_6H_4(NO_2).CH(OH).CHCl.CO_2H$. [165°]. Prepared in the same way from *p*-nitro-cinnamic acid (Beilstein a. Kuhlberg, *A.* 163, 142). Trimetric plates (from water). HCl (S.G. 1·1) at 150° gives chloro-nitro-cinnamic acid. Na_2CO_3Aq gives, on warming, *p*-nitro-β-oxy-cinnamic acid.

CHLORO-*o*-NITRO-PHENOL $C_6H_4ClNO_3$ *i.e.* $C_6H_3Cl(NO_2)(OH)$ [3:6:1]. Mol. w. 173½. [39°] (L.). [40° and 32½°] (U.).

Formation.—1. By boiling (3,6,1)-chloro-di-nitro-benzene with aqueous NaOH (Laubenheimer, *B.* 9, 768).—2. By nitrating *m*-chloro-phenol (Uhlemann, *B.* 11, 1161).

Properties.—Lemon-yellow needles or prisms (from water).

Salts.—$C_6H_3Cl(NO_2)(ONa)$: scarlet prisms, m. sol. cold water.—BaA'_2 aq: slender scarlet needles.—AgA'.

Methyl ether $C_6H_3Cl(NO_2)(OMe)$. [70·5°]. Needles.

Chloro-*o*-nitro-phenol $C_6H_3Cl(NO_2)(OH)$ [6:2:1]. [70°]. Formed, together with the isomeride [111°], by treating *o*-chloro-phenol with nitric acid (S.G. 1·36) diluted with an equal weight of water (Faust a. Müller, *A.* 173, 309). Flat yellow needles (from chloroform). Volatile with steam. HNO_3 gives chloro-di-nitro-phenol [111°].

Salts.—$C_6H_3Cl(NO_2)(OK)$: long dark-red needles, v. sol. water.—CaA'_2 aq: reddish-brown prisms, m. sol. water.—BaA'_2 aq: short copper-brown plates, sl. sol. water.—AgA': carmine-red scales, sl. sol. water.

Chloro-*o*-nitro-phenol $C_6H_3Cl(NO_2)(OH)$ [4:2:1]. [87°].

Formation.—1. The sole product of the action of dilute HNO_3 on *p*-chloro-phenol (Faust, *B.* 6, 132; *A.* 173, 317; *Suppl.* 7, 190; *Z.* [2] 5, 450). 2. By chlorination of *o*-nitro-phenol (Armstrong a. Prevost, *B.* 7, 922).—3. One of the products of the action of alcoholic KOH on (4,2,1)-chloro-di-nitro-benzene (Laubenheimer, *B.* 7, 1601).

Properties.—Light yellow monoclinic prisms (from $CHCl_3$). V. sl. sol. water, m. sol. alcohol. Volatile with steam. Br and water at 100° give chloro-bromo-nitro-phenol [125°] (Ling, *C. J.* 51, 786). But Br in HOAc gives an isomeric chloro-bromo-nitro-phenol [120°].

Salts.—$C_6H_3Cl(NO_2)(ONH_4)$: orange-red needles.—NaA' aq: red prisms.—BaA'_2 4aq: short red prisms.—AgA'.

Ethyl ether $C_6H_3Cl(NO_2)(OEt)$. [62°]. From AgA' and EtI. Formed also by nitrating the ethyl ether of *p*-chloro-phenol (Hallock, *Am.* 2, 258; *B.* 14, 37).

Chloro-*p*-nitro-phenol $C_6H_3Cl(NO_2)(OH)$ [2:4:1]. [111°].

Formation.—1. By chlorinating *p*-nitro-phenol (Armstrong, *C. J.* 25, 12; Faust a. Müller, *A.* 173, 309; Kollrepp, *A.* 234, 4).—2. Together with the isomeride [70°], by treating *o*-chloro-phenol with dilute HNO_3 (F. a. M.).—3. From chloro-di-nitro-phenol [111°] by reduction to chloro-nitro-amido-phenol followed by displacement of NH_2 by Cl through the diazo- reaction (Faust, *Z.* 1871, 339).

Properties.—White silky needles, m. sol. boiling water, v. sol. alcohol, ether, and chloroform. Very slightly volatile with steam. HNO_3 converts it into chloro-di-nitro-phenol [111°].

Salts.—$C_6H_3Cl(NO_2)(OK)$aq: brown needles, v. sol. water.—CaA'_2 4aq: tufts of canary-yellow needles, v. sol. water.—BaA'_2 7aq: long dark-yellow needles.—AgA': copper-brown flattened needles, sl. sol. water.

Methyl ether $C_6H_3Cl(NO_2)(OMe)$. From the methyl ether of nitro-*o*-amido-phenol by displacement of NH_2 by Cl. Needles.

Ethyl ether $C_6H_3Cl(NO_2)(OEt)$. *Chloro-nitro-phenetol.* [78°]. Formed by chlorinating the ethyl ether of *p*-nitro-phenol by HCl and $KClO_3$ (Hallock, *B.* 14, 37; *Am.* 3, 21).

Chloro-nitro-phenol. *Methyl ether* $C_6H_3Cl(NO_2)(OMe)$ [2:*x*:1]. *Chloro-nitro-anisol.* [94°]. Prepared by nitration of the methyl ether of *o*-chloro-phenol (Fischli, *B.* 11, 1461). Colourless spikes.

Chloro-di-nitro-phenol $C_6H_2Cl(NO_2)_2(OH)$ [4:2:6:1]. [81°].

Formation.—1. From *p*-chloro-phenol and HNO_3 (S.G. 1·4) (Dubois, *Z.* 1867, 205).—2. By nitration of *p*-chloro-phenol sulphonic acid (Petersen a. Praderi, *A.* 157, 156).—3. By nitrating chloro-nitro-phenol [87°] (Faust a. Saame).—4. From di-chloro-di-nitro-benzene [104°] and boiling aqueous NaOH (Engelhardt a. Latschinoff, *Z.* 1870, 234; Körner, *G.* 4, 395).—5. By chlorinating ('β')-di-nitro-phenol (Armstrong, *B.* 6, 649).—6. In small quantity, together with the isomeride [111°], by the action of ICl on tri-nitro-phenol (picric acid) (Petersen, *B.* 6, 369; Armstrong, *loc. cit.*).—7. By boiling chloro-di-nitro-aniline [145°] with aqueous KOH (Korner). 8. By dissolving chloro-*o*-oxy-benzoic acid in fuming HNO_3 (Smith a. Peirce, *A. Ph. S.* 17, 707; *Am.* 1, 176; *B.* 13, 35).

Properties.—Yellow monoclinic prisms (from chloroform). Sl. sol. hot water, v. sol. alcohol. Combines with aniline, forming $C_6H_4ClN_2O_5NH_2C_6H_5$ [187°] (S. a. P.); decomposed by boiling water.

Salts. $C_6H_2Cl(NO_2)_2(OK)$: long red needles with green lustre; v. sol. hot, v. sl. sol. cold water. NH_4A': deep orange needles.—$NaA'3aq$: scarlet moss-like forms.—BaA'_2aq: pale, saffron-yellow needles, v. sl. sol. hot water.—$CuA'_2 2aq$: saffron-yellow needles. PbA'_2aq: yellow needles. AgA': red needles.

Methyl ether $C_6H_2Cl(NO_2)_2(OMe)$: [65°].

Ethyl ether $C_6H_2Cl(NO_2)_2(OEt)$: [55°].

Chloro-di-nitro-phenol $C_6H_2Cl(NO_2)_2(OH)$. [80°]. Formed, together with the preceding, with which it is perhaps identical, by nitrating chloro-*o*-oxy-benzoic acid (Smith a. Peirce, *A. Ph. S.* 17, 707). Solidifies at 25°, whereas the preceding solidifies at 69°.—$KA'1\frac{1}{2}aq$: orange needles, much more soluble in water than the K salt of the preceding. AgA': bronzed needles.

Chloro-di-nitro-phenol $C_6H_2Cl(NO_2)_2(OH)$ [2:4:6:1]. [111°] (F. a. S.); [96°] (Zehenter, *M.* 6, 527). S. ·052 at 10°.

Formation.—1. From *o*-chloro-phenol and conc. HNO_3 (Griess, *A.* 109, 286; Armstrong, *C. J.* 25, 96; Faust a Müller, *A.* 173, 312).—2. From *o*- or *p*-nitro-phenol by successive chlorination and nitration (Faust a. Saame, *A. Suppl.* 7, 195; Seifart, *A. Suppl.* 7, 198).—3. The chief product of the action of ICl on picric acid (Petersen, *B.* 6, 368). 4. By chlorinating di-nitro-phenol [114°] (Armstrong, *C. J.* 25, 12; Faust, *Z.* 1871, 339).—5. By nitrating (2,4,1)-chloro-nitro-phenol (Armstrong; F. a. M.). 6. By nitrating (2,6,1)-chloro-nitro phenol (F. a. M.).—7. From di-nitro-amido-phenol (picramic acid), by displacing NH_2 by Cl through the diazo-reaction (F.).—8. By the action of HNO_3 on di-chloro-phenol *p*-sulphonic acid (Armstrong, *C. J.* 24, 1112).—9. From di-chloro-*p*-nitro-phenol and HNO_3 (A.). 10. By nitrating *o*-chloro-phenol sulphonic acid (Armstrong a. Prevost, *B.* 7, 405).

Properties.—Yellowish laminæ (from alcohol) or irregular six-sided tables (from $CHCl_3$). Sl. sol. hot water, m. sol. alcohol and ether. Tastes bitter.

Salts.—$C_6H_2Cl(NO_2)_2(OK)aq$: short slender yellow needles.—$NaA'1\frac{1}{2}aq$: short yellow needles.—$NH_4A'1\frac{1}{2}aq$.—NH_4A' (G.).—$NH_4A'aq$ (F. a S.).—$BaA'_2 9aq$ (F. a. S.).—$BaA'_2 10aq$ (F. a. M.).—$CaA'_2 7aq$: flat golden needles.—$MgA'_2 7aq$.—$MgA'_2 10aq$. $CuA'_2 8aq$: greenish-yellow hair-like needles.—$AgA'aq$.

Chloro-di-nitro-phenol $C_6H_2Cl(NO_2)_2(OH)$. [70°]. From di-chloro-di-nitro-benzene and aqueous NaOH (Engelhardt a. Latschinoff, *Z.* 1870, 234; Körner, *G.* 4, 395). Long needles.—$BaA'_2 3aq$: yellow needles.

Di-chloro-nitro-phenol $C_6H_2Cl_2(NO_2)(OH)$ [2:4:6:1]. [122°].

Formation.—1. By nitrating di-chloro-phenol [43°] (Fischer, *A. Suppl.* 7, 185; Chandelon, *B.* 16, 1752) or its sulphonic acid (Armstrong, *C. J.* 24, 1119; 25, 93). 2. By passing chlorine into an aqueous solution of *o*-nitro-phenol *p*-sulphonic acid (Schmitt a. Glutz, *B.* 2, 52).—3. By chlorinating chloro-nitro-phenol [87°] (Faust a. Saame, *A. Suppl.* 7, 195).—4. From *o*-chloro-phenol by successive nitration and chlorination (A.).—5. By chlorinating chloro-nitro-phenol sulphonic acid (A.).—6. From di-chloro-*o*-oxy-benzoic acid by dissolving in HOAc and treating with HNO_3 (Smith a. Knerr, *Am.* 8, 95).

Properties.—Yellow laminæ (from alcohol). Sl. sol. water, forming a deep yellow solution. V. sol. alcohol and ether. Volatile with steam. Explodes when heated suddenly. HNO_3 forms chloro-di-nitro-phenol [81°]. Bromine and water at 100° form chloro-tri-bromo-quinone (Ling, *C. J.* 51, 781).

Salts. — $C_6H_2Cl_2(NO_2)(ONH_4)$: orange needles; may be sublimed.—NaA': nodular groups of orange-red needles.—KA': needles of the colour of CrO_3. $KA'aq$ (Faust, *A.* 173, 317). $BaA'_2 2aq$: orange needles, v. sl. sol. water.—$MgA'_2 2aq$.—$PbA'(OH)$.—$ZnA'_2 2aq$.

Ethyl ether $C_6H_2Cl_2(NO_2)(OEt)$. [29°]. Pearly prisms.

Acetyl derivative $C_6H_2Cl_2(NO_2)(OAc)$. [77°]. From NaA' and AcCl.

Di-chloro-nitro-phenol $C_6H_2Cl_2(NO_2)(OH)$ [6:2:4:1]. [125°].

Formation.—1. By chlorinating *p*-nitro-phenol (Seifart, *A. Suppl.* 7, 198; Kollrepp, *A.* 234, 8).—2. By nitrating di-chloro-phenol sulphonic acid (Armstrong, *C. J.* 24, 1112; Faust, *Z.* 1871, 338).

Properties.—Slightly yellowish prisms or tables (from ether), or colourless needles (from chloroform). V. sl. sol. hot water, not volatile with steam. Converted by heat into di-chloro-quinone, NO, and N (Armstrong a. Brown, *B.* 7, 926). HNO_3 (S.G. 1·45) forms chloro-di-nitro-phenol [111°]. Bromine and water at 100° form di-chloro-di-bromo-quinone (Ling, *C. J.* 51, 786).

Salts.—$C_6H_2Cl_2(NO_2)(ONH_4)$ aq: shining yellow needles, becoming anhydrous and colourless over H_2SO_4.—$NaA'5aq$: yellow needles.—$KA'aq$: orange needles. $BaA'_2 3\frac{1}{2}aq$: red needles (Ling, *C. J.* 51, 786).—$BaA'_2 4aq$ (S.): brown-red laminæ or red needles. $BaA'_2 8aq$: yellow needles (F. a. M.; *A.* 173, 311).—$CaA'_2 9aq$: golden needles or laminæ, v. sol. water.—$CdA'_2 3\frac{1}{2}aq$.—$PbA'_2 4\frac{1}{2}aq$.—$CuA'_2 5aq$.—$MgA'_2 10aq$: rosettes of yellow needles. AgA': colourless needles.

Ethyl ether $C_6H_2Cl_2(NO_2)(OEt)$ [35°].

Di-chloro-nitro-phenol $C_6H_2Cl_2(NO_2)(OH)$. Formed in small quantity by nitrating di-chloro-phenol with $ClSO_3H$ (Armstrong, *Z.* 1871, 679). Short yellow needles (from water).

Tri-chloro-nitro-phenol $C_6HCl_3(NO_2)(OH)$ [6:4:2:3:1]. [69°]. Obtained by saponifying its nitro-benzoyl derivatives, which are obtained by nitrating benzoyl-tri-chloro-phenol (Daccomo, *B.* 18, 1164). Glistening colourless needles. V. sol. alcohol, ether, and benzene, sl. sol. water. Fe_2Cl_6 gives a violet-blue colouration.

Salts.—$A'NH_4$: small yellow needles.—$A'K$ aq.—$A'Ag$: small yellow needles.—A'_2Ba aq: yellow plates.

o-Nitro-benzoyl derivative $C_6HCl_3(NO_2).OCO.C_6H_4(NO_2)$: [106° cor.]; colourless glistening scales; sol. alcohol and ether.

m-Nitro-benzoyl derivative $C_6HCl_3(NO_2).OCO.C_6H_4(NO_2)$: [146° cor.]; large colourless tables; sol. alcohol and ether, insol. water.

Ethyl ether (?) [54°]. From tri-chloro-phenetol and cold H_2SO_4 and HNO_3 (Faust, *A.* 149, 152).

Tri-chloro-nitro-phenol $C_6HCl_3(NO_2)(OH)$ [2:3:5:4:1]. [146°]. From tri-chloro-phenol [54°] and HNO_3. White needles. Reduces to tri-chloro-*p*-amido-phenol (Lampert, *J. pr.* [2] 33, 382).

Ethyl ether $C_6HCl_3(NO_2)(OEt)$. [69°].

Tri-chloro-di-nitro-phenol. *Ethyl ether* $C_6Cl_3(NO_2)_2(OEt)$. [100°]. From tri-chloro-phenetol and warm HNO_3 mixed with H_2SO_4 (Faust, *A.* 149, 152).

CHLORO-NITRO-PHENOL SULPHONIC ACID $C_6H_2Cl(NO_2)(OH)(SO_3H)$ [2:6:1:4]. From di-chloro-phenol sulphonic acid and cold HNO_3 (Armstrong, *C. J.* 24, 1117). Formed also by nitrating *o*-chloro-phenol sulphonic acid (Armstrong a. Prevost, *B.* 7, 404). An isomeric acid is formed by chlorinating nitro-phenol sulphonic acid (Armstrong a. Brown, *C. J.* 25, 872). HNO_3 converts it into chloro-di-nitro-phenol [111°]. Chlorine forms di-chloro-nitro-phenol [121°].

Salts.—$C_6H_2ClNSO_6K_2$: orange-red six-sided plates, v. e. sol. hot water.—$C_6H_3ClNSO_6K\,\frac{1}{2}aq$: yellow needles.

DI-CHLORO-DI-NITRO-DIPHENYL $C_6H_3(NO_2)Cl.C_6H_3(NO_2)Cl$. [140°]. Prepared by the nitration of di-chloro-diphenyl. [4:1] $C_6H_4Cl.C_6H_4Cl$ [1:4] (Schmidt a. Schultz, *B.* 12, 494). Small needles or long prisms. Sl. sol. cold, v. sol. hot, alcohol, and C_6H_6.

CHLORO-NITRO-DI-PHENYL-AMINE $C_{12}H_9ClN_2O_2$ *i.e.* $C_6H_5.NH.C_6H_3Cl(NO_2)$. [109°]. Slowly formed, together with benzene-azo-aniline (amido-azo-benzene) by mixing (1,3,4)-chloro-di-nitro-benzene [39°] (1 mol.) with aniline (3 mols.) (Laubenheimer, *B.* 9, 771). Long red needles (from alcohol). Does not combine with acids.

Nitrosamine $C_6H_5.N(NO).C_6H_3Cl(NO_2)$. [111°]. Yellow, six-sided laminæ, m. sol. cold alcohol.

CHLORO-DI-NITRO-DI-PHENYL-AMINE-*o*-CARBOXYLIC ACID $C_6H_2(NO_2)_2Cl.NH.C_6H_4.CO_2H$ [256°]. Formed by mixing alcoholic solutions of di-chloro-di-nitro-benzene $C_6H_2Cl_2(NO_2)_2$[1:4:2:6] and anthranilic acid $C_6H_4(NH_2)CO_2H$[1:2] and adding NH_3 (Jourdan, *B.* 18, 1454). Glistening red prisms. Sol. hot alcohol and acetic acid, insol. water.

Chloro-di-nitro-di-phenyl-amine-*o*-carboxylic acid $C_6H_3(NO_2)_2.NH.C_6H_3Cl.CO_2H$. [282° uncor.]. Obtained by mixing alcoholic solutions of chloro-di-nitro-benzene $C_6H_3Cl(NO_2)_2$[1:2:4] and chloro-amido-benzoic acid $C_6H_3Cl(NH_2)CO_2H$[1:4:5], and adding NH_3 (Jourdan, *B.* 18, 1450). Fine orange needles. V. sl. sol. cold alcohol and acetic acid, insol. water, benzene, and ligroin. A'_2Ca: sl. sol. water.

TRI-CHLORO-DI-NITRO-DI-PHENYL-BUTANE $C_{16}H_{13}Cl_3(NO_2)_2$. From tri-chloro-di-phenyl-butane and fuming HNO_3 (Hepp, *B.* 7, 1420). Small yellowish tables (from alcohol). Sl. sol. CS_2, v. sol. ether.

CHLORO-NITRO-PHENYLENE-DIAMINE $C_6H_2Cl(NO_2)(NH_2)_2$[1:4:3:5]. [192°–194°]. From $C_6H_2Cl_3(NO_2)$[1:3:5:2] and alcoholic NH_3 at 200° for several days (Beilstein a. Kurbatoff, *A.* 192, 233). Red needles. V. sol. alcohol, sol. dilute (50 per cent.) acetic acid or benzene, sl. sol. light petroleum.

DI-CHLORO-NITRO-PHENYL-ETHANE *v.* DI-CHLORO-NITRO-ETHYL-BENZENE.

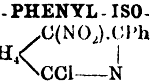
Penta-chloro-di-nitro-di-phenyl-ethane $C_{14}H_7Cl_5N_2O_4$ *i.e.* $CCl_3.CH(C_6H_3Cl.NO_2)_2$. [143°]. From $CCl_3.CH(C_6H_4Cl)_2$ and fuming HNO_3 (Zeidler, *B.* 7, 1181). Needles (from alcohol).

CHLORO-NITRO-PHENYL MERCAPTAN $C_6H_4ClNSO_2$ *i.e.* $C_6H_3Cl(NO_2)(SH)$ [3:6:1]. [171°]. From (3,6,1)-chloro-di-nitro-benzene and alcoholic KSH (Beilstein a. Kurbatoff, *A.* 197, 82). Yellow needles, v. sol. chloroform, v. sl. sol. alcohol.

Chloro-nitro-phenyl mercaptan $C_6H_3Cl(NO_2)(SH)$ [4:2:1]. [213°]. From (1,4,2)-di-chloro-nitro-benzene and alcoholic KSH (Beilstein a. Kurbatoff, *A.* 197, 79). Yellow tables (from HOAc). Sl. sol. alcohol. Alcoholic ammonium sulphide converts it into $C_{12}H_4Cl_2N_2S_2$ [147°], which crystallises in yellow needles, and is converted by HNO_3 into $C_6H_3ClN_2S$ [104°].

CHLORO-NITRO-PHENYL-*m*-PHENYLENE-DIAMINE $NH_2.C_6H_4.NH.C_6H_3Cl(NO_2)$. [151°]. Red needles. Sl. sol. cold alcohol. Prepared by warming an alcoholic solution of *m*-phenylene-diamine and (1,3,4)-chloro-di-nitro-benzene. Forms with acids unstable yellow salts (Laubenheimer, *B.* 11, 1158).

(*Py.* 4:1:2)-**CHLORO-NITRO-PHENYL-ISOQUINOLINE** $C_{15}H_9ClO_2N_2$ *i.e.*



$$C_6H_4\left\langle\begin{array}{l}C(NO_2).CPh\\ \qquad\qquad\;|\\ CCl\text{——}N\end{array}\right.$$

[156°]. Formed by heating nitro-oxy phenyl-isoquinoline (nitro-iso-benzal-phthalimidine) with $POCl_3$ (Gabriel, *B.* 19, 834). Small yellow needles or prisms. V. sol. hot acetic acid, benzene, chloroform, ether, and CS_2; sl. sol. alcohol, v. sl. sol. ligroin. By HI and P it is reduced to amido-phenyl-isoquinoline. Heated with alcoholic sodium ethylate it yields the ethyl-ether of nitro-oxy-phenyl-isoquinoline.

DI-CHLORO-DI-NITRO-DI-PHENYL-SULPHIDE $(C_6H_3Cl.NO_2)_2S$. [150°]. Yellow needles. Almost insol. alcohol, sl. sol. acetic acid. Prepared by the action of alcoholic K_2S on (1, 4, 6)-di-chloro-nitro-benzene (Beilstein a. Kurbatow, *B.* 11, 2056; *A.* 197, 79).

CHLORO-NITRO-PHENYL-*p*-TOLYL-AMINE $C_6H_4Me.NH.C_6H_3Cl(NO_2)$. [124°]. Small red needles. Sl. sol. cold alcohol. Prepared by the action of a cold alcoholic solution of *p*-toluidine on (1, 3, 4)-chloro-di-nitro-benzene (Laubenheimer, *B.* 11, 1157).

DI-CHLORO-DI-NITRO-DI-PHENYL-UREA $C_{13}H_8Cl_2N_4O_5$ *i.e.* $CO(NH.C_6H_3Cl.NO_2)_2$. [210°]. From di-chloro-di-phenyl-guanidine and HNO_3 (Losanitsch, *Bl.* [2] 32, 170). Yellow tables, insol. water, sl. sol. alcohol.

CHLORO-NITRO-PHTHALIC ACID $C_8H_4ClNO_6$ *i.e.* $C_6H_2Cl(NO_2)(CO_2H)_2$. From (γ)-di-chloro-naphthalene and HNO_3 (Atterberg, *B.* 10, 547).—K_2A'': crystals; explodes above 300°.

Di-chloro-nitro-phthalic acid. From (ζ)-tri-chloro-naphthalene and HNO_3 (S.G. 1·2) at 150° (Widmann, *B.* 12, 960).

Tri-chloro-nitro-phthalic acid $C_8H_2Cl_3NO_6$. From ('*a*')-tri-chloro-naphthalene and HNO_3 (Atterberg a. Widmann, *B.* 10, 1844).

DI-CHLORO-DI-NITRO-PROPANE $C_3H_4Cl_2(NO_2)_2$ (?). From di-chloro-propylene (from tri-chloro-butyric aldehyde) and fuming HNO_3 (Pinner, *A.* 179, 49). Oil; converted by tin and HCl into $C_3H_5Cl_3$ (1 9°), $C_3H_4Cl_2(NH_2)$, and tri-chloro-nitro-propane

Tri-chloro-nitro-propane $C_3H_4Cl_3(NO_2)$. (c. 193°). Formed as above.

DI-CHLORO-NITRO-PROPYLENE $C_3H_3Cl_2(NO_2)$. (c. 159°). Formed by the action of aqueous NaOH upon di-chloro-di-nitro-propane and upon tri-chloro-nitro-propane (Pinner, *A.* 179, 57).

CHLORO-NITRO-QUINOLINE $C_9H_5Cl(NO_2)N$ [120° 123°]. Formed, together with the isomeride [186°], by nitration of (*B.* 1 or 3)-chloro-quinoline (La Coste a. Bodewig, *B.* 17, 927). V. sol. hot alcohol, sl. sol. water.

Chloro-nitro-quinoline $C_9H_5Cl(NO_2)N$. [186°]. Formed, together with the preceding, by nitration of (*B.* 1 or 3)-chloro-quinoline (La Coste a. Bodewig, *B.* 17, 927). Long colourless needles. Sl. sol. alcohol.

CHLORO-NITRO-QUINONE *Anilide* $C_6HCl(NO_2)(NHPh)O_2$ [6 or 2:3:2 or 6:4:1]. [208°]. Small red trimetric tables. Formed by the action of aniline in alcoholic solution upon di-chloro-nitro-quinone $C_6HCl_2(NO_2)O_2$ [6:2:3:4:1] (Guareschi a. Daccomo, *B.* 18, 1172).

Di-chloro-nitro-quinone $C_6HCl_2(NO_2)O_2$ [6:2:3:4:1]. [220°]. Formed by the action of a mixture of HNO_3 and H_2SO_4 upon the propionyl derivative of tri-chloro-phenol (Guareschi a. Daccomo, *B.* 18, 1171). Small yellow needles. Sol. cold alcohol, sl. sol. ether and CS_2, v. sl. sol. hot water.

CHLORO-ISO-NITROSO-ACETIC ETHER $N(OH).CCl.CO_2Et$(?). *Chloro-oximido-acetic ether.* [80°]. From chloro-aceto-acetic ether (*v.* Allihn, *B.* 11, 567) and fuming HNO_3 (Pröpper, *A.* 222, 50). Glittering columns (from ether). V. e. sol. alcohol and ether. Boiling water splits it up into hydroxylamine, oxalic acid, and alcohol.

CHLORO-ISO-NITROSO-ACETONE $CH_3.CO.CCl(NOH)$. *Mono-oxim* of *ω-chloro-pyruvic aldehyde.* [110°]. Formed in small quantity by treating chloro-acetone with fuming HNO_3 (Glutz, *Z.* 1870, 529; Barbaglia, *B.* 6, 321). Formed also by heating the product of the action of nitrous acid gas upon acetone ($(CH_3)_2C(ONO_2).C(NOH).CO.CH_3$(?)), with dilute HCl; acetone and HNO_2 are formed at the same time (Sandmeyer, *B.* 20, 640). Prisms or tables; v. sol. water, alcohol, and ether.

Oxim $CH_3.C(NOH).CCl(NOH)$. ***Di-oxim of ω-chloro-pyruvic aldehyde. Chloro-methyl-glyoxim.*** [171°]. Small white needles.

a-CHLORO-*o*-NITRO-STYRENE $C_8H_6ClNO_2$ ***i.e.*** $C_6H_4(NO_2).CCl:CH_2$. ***Nitro-phenyl-chloro-ethylene.*** From *o*-nitro-acetophenone and PCl_5 (Gevekoht, *A.* 221, 329). Oil.

a-Chloro-*p*-nitro-styrene $C_6H_4(NO_2).CCl:CH_2$ [64°]. From *p*-nitro-acetophenone and PCl_5 (Drewson, *A.* 212, 162). Concentric groups of slender needles (from benzoline).

a-Chloro-ω-nitro-styrene $Ph.CCl:CH.NO_2$ [49°]. From $PhCHCl.CHCl.NO_2$ and aqueous NaOH (Priebs, *A.* 225, 345). Golden plates (from light petroleum). Insol. water, soluble, when finely divided, in alkalis.

ω-Chloro-*o*-nitro-styrene $C_6H_4(NO_2).CH:CHCl$. [59°]. Formed as a by-product in the preparation of chloro-*o*-nitro-oxy-phenyl-propionic acid by the action of hypochlorous acid on *o*-nitro-cinnamic acid (Lipp, *B.* 17, 1070). Glistening needles or prisms. V. sol. ether and hot alcohol, sl. sol. hot water, insol. cold water.

TRI-CHLORO-NITRO-THIOPHENE $C_4SCl_3(NO_2)$. [86°] Formed by nitration of tri-chloro-thiophene. Reddish-yellow felted needles. V. sol. benzene and ether, less in alcohol (Rosenberg, *B.* 12, 652).

CHLORO-NITRO-TOLUENE $C_6H_3(CH_3)Cl(NO_2)$ [1:4:3]: [9°]. (260° i. V.). S.G. $\frac{22}{22}$ 1·297.

Formation.—1. Together with the (1:2:4)-isomeride by nitration of *p*-chloro-toluene (10 pts.) with a cold mixture of conc. HNO_3 (12 pts.) and conc. H_2SO_4 (17 pts.) (Engelbrecht, *B.* 7, 797; Goldschmidt a. Hönig).—2. From *m*-nitro-*p*-toluidine $C_6H_3(CH_3)(NO_2)(NH_2)$ [1:3:4] by the action of Cu_2Cl_2 upon the diazo- compound (Gattermann a. Kaiser, *B.* 18, 2599).

Reaction.—On reduction it gives *p*-chloro-*m*-toluidine [28°] (Goldschmidt a. Hönig, *B.* 19, 2438).

(*a*)-Chloro-nitro-toluene $C_6H_3(CH_3)Cl(NO_2)$ [1:2:*x*]. (250°). Oil. Formed by nitration of *o*-chloro-toluene. On reduction it gives a chloro-toluidine [83°] (Goldschmidt a. Hönig, *B.* 19, 2443; *cf.* Wroblewsky, *A.* 168, 200).

Chloro-nitro-toluene $C_6H_3(CH_3)Cl(NO_2)$[1:4:2]. [38°]. (240° at 718 mm.).

Formation.—1. Together with the [1:3:4] isomeride, by nitration of *p*-chloro-toluene (10 pts.) with a cold mixture of conc. HNO_3 (12 pts.) and conc. H_2SO_4 (17 pts.) (Engelbrecht, *B.* 7, 797; Goldschmidt a. Hönig, *B.* 19, 2438).—2. From *o*-nitro-*p*-toluidine by the action of Cu_2Cl_2 upon the diazo- compound (Beilstein a. Kuhlberg, *A.* 158, 336).

Properties.—Needles; sl. sol. cold alcohol, volatile with steam. On reduction it gives *p*-chloro-*o*-toluidine [22°] (Goldschmidt a. Hönig, *B.* 19, 2438).

Chloro-nitro-toluene $C_6H_3MeCl(NO_2)$ [1:2:5] [41°]. (248°) at 711 mm. Obtained by the action of Cu_2Cl_2 upon diazotised nitro-*o*-toluidine $C_6H_3Me(NH_2)(NO_2)$ [1:2:5]. Needles (from ether) (Goldschmidt a. Hönig, *B.* 20, 199).

Chloro-nitro-toluene $C_6H_3(CH_3)Cl(NO_2)$ [1:3:5]. [55°]. Formed from *m*-nitro-*m*-toluidine $C_6H_3Me(NO_2)NH_2$ [1:3:5] by the action of cuprous chloride upon the diazo- compound. Yellow needles (from alcohol). Volatile with steam (Hönig, *B.* 20, 2419).

Chloro-nitro-toluene $C_6H_3(CH_3)(Cl)(NO_2)$ [1:2:4]. [65½°]. Formed by the action of PCl_5 on *p*-nitro-toluene (Lellmann, *B.* 17, 534; *cf.* Wachendorff, *A.* 185, 273). Colourless crystals. V. sol. alcohol. Volatile with steam. On reduction it gives chloro-*p*-toluidine [26°] (238°).

Chloro-di-nitro-toluene $C_6H_2(CH_3)Cl(NO_2)_2$ [1:4:3:5]. [48°]. Formed by nitration of chloro-nitro-toluene $C_6H_3(CH_3)Cl(NO_2)$ [1:4:3]. Long white needles (Hönig, *B.* 20, 2420).

Chloro-di-nitro-toluene $C_6H_2(CH_3)(NO_2)_2Cl$ [1:2?:6?:4]. [76°]. Small yellow needles (from ether). Formed by nitration of *p*-chloro-toluene with fuming HNO_3 (Goldschmidt a. Hönig, *B.* 19, 2439).

Chloro-di-nitro-toluene $C_6H_2(CH_3)Cl(NO_2)_2$ [1:4:2:6]. [101°]. Formed by nitration of *p*-chloro-*o*-nitro-toluene $C_6H_3(CH_3)(NO_2)Cl$[1:2:4]. Long white needles (Hönig, *B.* 20, 2420).

Di-chloro-nitro-toluene $C_6H_2(CH_3)Cl_2(NO_2)$. [-14°]. (274°). S.G. ^{17} 1·455. From di-chloro-toluene and fuming HNO_3 (Wroblewsky, *A.* 168, 212). Oil.

(β)-**Di-chloro-nitro-toluene** $C_6H_2(CH_3)Cl_2(NO_2)$ [1:2:4:?]. [53°]. Formed by the action of conc. HNO_3 on (α)-dichlorotoluene (Seelig, *A.* 237, 163). Long needles (from methyl alcohol).

(α)-**Di-chloro-di-nitro-toluene** $C_6H(CH_3)Cl_2(NO_2)_2$ [1:2:3:?:?]. [122°]. Formed by the action of HNO_3 (2 pts.) and H_2SO_4 (1 pt.) on (α)-di-chloro-toluene (10 pts.) (Seelig, *A.* 237, 163). Needles (from methyl alcohol). Yields on reduction a diamine which is apparently meta.

(β)-**Di-chloro-di-nitro-toluene** $C_6H(CH_3)Cl_2.(NO_2)_2$ [1:2:4:5:6]. [102°]. Formed by the action of a mixture of HNO_3 (2 pts.) and H_2SO_4 (1 pt.) on (β)-chloro-toluene (10 pts.) (Seelig, *A.* 237, 163). Needles.

(α)-**Tri-chloro-nitro-toluene** $C_6H(CH_3)Cl_3(NO_2)$. [92°]. S. (alcohol) 4·5 at 20° (Schultz, *A.* 187, 277). Formed by dissolving (α)-trichlorotoluene in conc. HNO_3 (Seelig, *A.* 237, 139; *B.* 18, 422; Beilstein a. Kuhlberg, *A.* 152, 240). Colourless plates (from alcohol).

(β)-**Tri-chloro-nitro-toluene** $C_6H(CH_3)Cl_3(NO_2)$. [60°]. Formed by dissolving (β)-trichlorotoluene in conc. HNO_3 (Seelig, *A.* 237, 140). Long yellow needles.

(α-) **Tri-chloro-di-nitro-toluene** $C_6(CH_3)Cl_3(NO_2)_2$. [227°]. Formed by warming (α)-trichlorotoluene with a mixture of conc. HNO_3 and H_2SO_4 (Schultz, *A.* 187, 280; Seelig, *A.* 237, 140; *B.* 18, 422). White plates or needles; v. sl. sol. alcohol. Reduced by tin and HCl to tri-chloro-tolylene-*p*-diamine.

(β-) **Tri-chloro-di-nitro-toluene** $C_6(CH_3)Cl_3(NO_2)_2$. [141°]. Formed by warming (β)-trichlorotoluene with a mixture of conc. HNO_3 and H_2SO_4 (Seelig, *A.* 237, 140; *B.* 18, 422). Light yellow needles, sl. sol. alcohol. Alcoholic NH_3 at 100° gives tri-chloro-nitro-toluidine [191°].

CHLORO - NITRO - TOLUENE SULPHONIC ACID $C_7H_6ClNSO_5$ *i.e.* $C_6H_2(CH_3)Cl(NO_2)(SO_3H)$. From liquid (α)-chloro-nitro-toluene and fuming sulphuric acid (Wroblewsky, *A.* 168, 204).—BaA'_2 4aq: needles, sl. sol. water.

(α)-**TRI-CHLORO-NITRO-TOLUIDINE** $C_6(CH_3)(NO_2)Cl_3(NH_2)$. [191°]. Formed by the action of alcoholic NH_3 upon tri-chloro-di-nitro-toluene [227°] (Seelig, *B.* 18, 423; *A.* 237, 140). Orange-yellow needles (from alcohol).

(β)-**Tri-chloro-nitro-toluidine** $C_6(CH_3)(NO_2)Cl_3(NH_2)$. [192°]. Formed by the action of alcoholic NH_3 upon tri-chloro-di-nitro-toluene [141°] (Seelig, *B.* 18, 423). Orange-red needles (from alcohol).

TRI - CHLORO - DI - NITRO - DI - TOLYL-ETHANE $C_{16}H_{12}Cl_3(NO_2)_2$. [122°]. From tri-chloro-di-tolyl-ethane $(C_7H_7)_2CH.CCl_3$ and fuming HNO_3 (O. Fischer, *B.* 7, 1191). Short yellowish prisms.

DI-ω-CHLORO-NITRO-XYLENE $C_6H_3(NO_2)(CH_2Cl)_2$. [45°]. From di-ω-chloro-*p*-xylene and fuming HNO_3 (Grimaux, *Z.* 1871, 598). Small plates. V. sol. ether.

Di-chloro-di-nitro-xylene $C_6(CH_3)_2Cl_2(NO_2)_2$. [225°]. Formed by nitrating di-chloro-*p*-xylene (Kluge, *B.* 18, 2098). Needles.

CHLORO-OCTANE *v.* Octyl chloride.

Di-chloro-octane $C_8H_{16}Cl_2$ *i.e.* $C_6H_{13}.CCl_2.CH_3$. (c. 195°). From methyl hexyl ketone and PCl_5 (Dachauer, *A.* 106, 271).

Di-chloro-octane $C_8H_{16}Cl_2$. (c. 199°). From Cl and the octylene from castor oil (D.; *cf.* Béhal, *Bl.* [2] 47, 33).

Di-chloro-octane $C_8H_{16}Cl_2$. (c. 235°). Formed by the action of Cl on a mixture of octylene and octane derived from paraffin (Thorpe a. Young, *A.* 165, 16).

CHLORO-OCTYL ALCOHOL $C_8H_{17}ClO$. S.G. ^{0} 1·003; ^{21} ·987. From octylene and very dilute ($\frac{1}{4}$ p.c.) aqueous HOCl (De Clermont, *Z.* 1870, 411). Oil.

CHLORO-OCTYL-BENZENE $C_6H_4(C_8H_{17})Cl$. (270°–275°). Formed by chlorination of octyl-benzene in presence of a trace of iodine. Oil. V. sol. alcohol and ether, insol. water (Ahrens, *B.* 19, 2719).

CHLORO-OPIANIC ACID *v.* Opianic acid.

TRI-CHLORO-ORCIN (?) $C_7H_5Cl_3O_2$ *i.e.* $C_6(CH_3)Cl_3(OH)_2$. [59°]. From orcin and Cl (Schunck, *A.* 54, 271) or HCl and $KClO_3$ (De Luynes, *A.* 130, 34). Slender needles.

Tri-chloro-orcin $C_6(CH_3)Cl_3(OH)_2$. [123°]. From the pentachloride, HI, and phosphorus (Stenhouse, *Tr.* 1848, 88; *Pr.* 20, 72). Needles (from water) or plates (from HOAc), m. sol. CS_2, m. sol. benzene, v. e. sol. alcohol and ether. Volatile with steam. HIAq and phosphorus at 180° convert it into orcin. K_3FeCy_6 oxidises it to di-chloro-oxy-toluquinone [157°].

Penta - chloro - orcin $C_6(CH_3)Cl_3(OCl)_2$ or $C_6(CH_3)Cl(Cl_2)_2O_2$. [120·5°]. According to Stenhouse, this, and not tri-chloro-orcin, is formed by treating orcin with $KClO_3$ and HCl. Prisms (from CS_2). M. sol. CS_2 and benzene, v. sol. ether. Boiling water or alcohol decompose it with formation of tri-chloro-orcin. Liberates iodine from KI, and gives a pp. of AgCl with $AgNO_3$ (Liebermann a. Dittler, *A.* 160, 265).

Compound $C_6(CH_3)Cl_3(OCl)_2HClO$. [140·5°]. From orcin, calcium hypochlorite, and HCl. Prisms (from benzene). V. sol. ether, sl. sol. CS_2. Converted by NH_3 into $C_6H_5Cl_3NO$ [187°] (Stenhouse, *B.* 6, 575).

CHLORO-OXALAMYLINE *v.* Chloro-iso-butyl-isoamyl-glyoxaline.

CHLORO-OXALETHYLINE *v.* Chloro-methyl-ethyl-glyoxaline.

CHLORO-OXALMETHYLINE *v.* Chloro-methyl-glyoxaline.

CHLORO-OXALPROPYLINE *v.* Chloro-ethyl-propyl-glyoxaline.

CHLORO-OXETHOSE C_4Cl_6O. (210°). S.G. ^{21} 1·652. Formed from alcoholic K_2S and perchlorinated ether:

$$C_4Cl_{10}O + 2K_2S = 4KCl + S_2 + C_4Cl_6O$$

(Malaguti, *A. Ch.* [3] 16, 19). Oil; smells like meadow-sweet. Has a sweet taste.

Reactions.—1. In sunlight it re-combines with *chlorine* $C_4Cl_6O + 2Cl_2 = C_4Cl_{10}O$.—2. *Chlorine water* forms trichloracetic acid.

CHLORO - OXIMIDO - ACETIC ETHER *v.* CHLORO-ISONITROSO-ACETIC ETHER.

CHLORO-OXINDOLE *v.* OXINDOLE.

Chloro-oxindole chloride *v.* DI-CHLORO-INDOLE.

CHLORO-DI-OXY-ACETIC ACID *Chloro-glyoxylic acid.*

Diethyl derivative of the Nitrile $ClC(OEt)_2CN$. (c. 160°). Obtained, impure, from $CCl_2(OEt)CN$ and NaOEt (Bauer, *A.* 229, 176). Polymerises.

Dipropyl derivative of the Nitrile $ClC(OPr)_2CN$. (c. 201°). From $CCl_2(OPr)CN$ and NaOPr. Polymerises.

TETRA - CHLORO - TETRA - OXY - ADIPIC ETHER. *Anhydride* $C_{10}H_{10}Cl_4O_8$ *i.e.* $EtO_2C.CCl_2.CO.CO.CCl_2.CO_2Et$. *Oxalyl-di-chloro-acetic ether.* [93°]. Formed by the action of chlorine upon di-oxy-quinone-di carboxylic ether. Slightly greenish prisms. By hot alcoholic NH_3 it is split up into 1 mol. of oxamide and 2 mols. of di-chloro-acetamide (Hantzsch a. Lœwy, *B.* 19, 26, 2385; Hantzsch a. Zeckendorf, *B.* 20, 1308).

DI-CHLORO-DI-OXY-DI-AMIDO-BENZENE *v.* DI-CHLORO-DI-AMIDO-HYDROQUINONE.

DI - CHLORO - DI - OXY - AMIDO - PYRIDINE $C_5H_4Cl_2O_2N_2$ probably $N\begin{matrix}\diagup C(OH)=CCl \diagdown \\ \diagdown C(OH)-CCl \diagup\end{matrix}C.NH_2$. *Di-chloro-glutazine.* [242°]. Formed in small quantity, together with tri-chloro-oxy amido-pyridine, tri-chloro-amido-pyridine, and tetra-chloro-amido-pyridine, by heating glutazine with PCl_5 (6 or 7 pts.). Short flat colourless needles. Sl. sol. hot water and alcohol. Dissolves readily in aqueous acids and alkalis. Combines with bromine (Stokes a. Pechmann, *B.* 19, 2710; *Am.* 8, 391).

Di-ethyl derivative $N\begin{matrix}\diagup C(OEt):CCl \diagdown \\ \diagdown C(OEt).CCl \diagup\end{matrix}C.NH_2$: [98°]. Long colourless needles. Readily sublime. Volatile with steam. V. sol. alcohol and ether, insol. water. Formed together with the mono-ethyl derivative by heating tetra-chloro-amido-pyridine with an excess of sodium ethylate at 190° for 3 or 4 hours.

Mono-ethyl derivative $N\begin{matrix}\diagup C(OH):CCl \diagdown \\ \diagdown C(OEt).CCl \diagup\end{matrix}C.NH_2$: [162°]. Flat needles. Sublimable. Not volatile with steam. V. sol. alcohol and ether, sl. sol. hot water. Dissolves in alkalis, but not in dilute acids. It is also formed by heating tri-chloro-oxy-amido-pyridine with sodium ethylate.—A'Na: glistening rhombic tables (Stokes a. Pechmann, *B.* 19, 2710; *Am.* 8, 396).

TRI - CHLORO - OXY - AMIDO - PYRIDINE $C_5H_3Cl_3N_2O$ probably $N\begin{matrix}\diagup C(OH):CCl \diagdown \\ \diagdown CCl-CCl \diagup\end{matrix}C.NH_2$. [282°]. Formed, together with an equal quantity of tetra-chloro-amido-pyridine and small quantities of di-chloro-di-oxy-amido-pyridine and tri-chloro-amido-pyridine, by heating glutazine with PCl_5 (6 to 7 pts.). Flat colourless needles. Sublimable. V. sol. hot water, nearly insol. cold, m. sol. hot alcohol, sl. sol. cold, sl. sol. ether and benzene, insol. ligroin. Monobasic acid, decomposes soluble carbonates. Dissolves in conc. HCl or conc. H_2SO_4, but is reprecipitated on dilution.—A'Na *x*aq: needles, m. sol. cold water.

Ethyl derivative $N\begin{matrix}\diagup C(OEt):CCl \diagdown \\ \diagdown CCl-CCl \diagup\end{matrix}C.NH_2$: [82°]. Colourless needles. Very volatile with steam. Peculiar odour. V. sol. alcohol, ether, etc. Formed by ethylation of the above, or by heating tetra-chloro-amido-pyridine with sodium ethylate (Stokes a. Pechmann, *B.* 19, 2710; *Am.* 8, 392).

γ-CHLORO-α-OXY-ANGELIC ACID $C_5H_7ClO_3$ *i.e.* $CH_3.CCl:CH.CH(OH).CO_2H$. [116°]. From tri-chloro-oxy-valeric acid, zinc, and HCl (Pinner a. Bischoff, *A.* 179, 100; Pinner a. Klein, *B.* 11, 1496). V. sol. water, alcohol, and ether, sl. sol. CS_2. Combines with Br. PCl_5 gives $CH_3.CCl:CH.CHCl.COCl$. — ZnA'_2. — CuA'_2. — AgA': needles, m. sol. cold water.

Ethyl ether EtA'. (230°).

Isobutyl ether $CH_2Pr.A'$. (c. 238°).

CHLORO-DI-OXY-ANTHRAQUINONE $C_{14}H_7ClO_4$. *Chloro-alizarin.* [244°-248°]. Prepared by the action of Cl on a cold solution of alizarin in CS_2 (Diehl, *B.* 11, 187). Sublimes in red needles. Sol. boiling, sl. sol. cold, water.

Di-chloro-di-oxy-anthraquinone $C_{14}H_6Cl_2O_4$. *Di-chloro-alizarin.* [208°-210°]. Prepared by the action of $SbCl_5$ on alizarin (Diehl, *B.* 11, 188). Sublimes in beautiful orange-red spikes. Combines with mordants readily, the colours resembling those produced by nitro-alizarin.

Tetra-chloro-di-oxy-anthraquinone $C_{14}H_2(OH)_2Cl_4O_2$. *Tetra-chloro alizarin.* [c. 260°]. Prepared by the action of $SbCl_5$ on alizarin (Diehl, *B.* 11, 189). Further action of $SbCl_5$ forms C_6Cl_6, C_2Cl_6, CCl_4, and CO_2. Reddish-brown crystalline powder. Does not combine with mordants.

CHLORO-OXY-BENZAMIDE *v.* AMIDE OF CHLORO-OXY-BENZOIC ACID.

DI-CHLORO-TETRA-OXY-BENZENE $C_6Cl_2(OH)_4$. *Hydrochloranilic acid.* From di-chloro-di-oxy-quinone by reduction with aqueous SO_2 at 100°, or with tin and HCl (Koch, *Z.* 1868, 203; Graebe, *A.* 146, 32). Needles. V. sol. water, alcohol, and ether. Oxidised by moist air into di-chloro-di-oxy-quinone (chloranilic acid).

Tetra-acetyl derivative $C_6Cl_2(OAc)_4$. [235°].

CHLORO-*o*-OXY-BENZOIC ACID $C_7H_5ClO_3$ *i.e.* $C_6H_3Cl(OH).CO_2H$ [5:2:1]. *Chloro-salicylic acid.* Mol. w. 175½. [172.5°] (H. a. B.); [168°] (V.). S. ·09 at 20°; 1·25 at 100°.

Formation.—1. By passing the calculated quantity of chlorine into salicylic acid dissolved in a large quantity of CS_2 (Hübner a. Brenken, *B.* 6, 174; *cf.* Cahours, *A. Ch.* [3] 13, 106), or in HOAc (Smith, *B.* 11, 1226; Marshall, *A. Ph. S.* 17, 476).—2. From (5,2,1)-chloro-amido-benzoic acid by displacement of NH_2 by OH through the diazo- reaction (Hübner a. Weiss, *B.* 6, 175).—3. From (2,5,1)-oxy-amido-benzoic acid by displacement of NH_2 by Cl (Schmitt, *Z.* 1864, 321; Beilstein, *B.* 8, 816).—4. From *p*-chloro-phenol, CCl_4, and alcoholic KOH (Hasse, *B.* 16, 2196).—5. From $C_6H_4Cl(ONa)$ [1:4] and CO_2 at 150° (Varnholt, *J. pr.* [2] 36, 20).

Properties.—Needles (from water). V. sol. alcohol, ether, and benzene. Fe_2Cl_6 colours its aqueous solution red.

Salts.—NaA'.—LiA' 2aq.—KA'.—BaA'$_2$ 3aq. CaA'$_2$ 3aq.—PbA'$_2$.—CuA'$_2$.—AgA'.

Methyl ether MeA'. [48°]. (249°). Needles.

Ethyl ether EtA'. [110°]. Needles.

Acetyl derivative $C_6H_3Cl(OAc).CO_2H$ [149°].

Amide $C_6H_3Cl(OH)(CONH_2)$ [223°].

Chloro-oxy-benzoic acid $C_6H_3Cl(OH).CO_2H$ [3:2:1]. [178°]. S. ·08 at 3·5°. From [2:1] $C_6H_4Cl(ONa)$ and CO_2 at 150° (Varnholt, *J. pr.* [2] **36, 22**). Long needles, volatile with steam, may be sublimed. V. sol. alcohol and chloroform. Fe_2Cl_6 gives a violet colour.—NaA'.—BaA'$_2$ 3aq.

Methyl ether MeA'. [83°]. (260°). Needles.

Chloro-oxy-benzoic acid $C_6H_3Cl(OH).CO_2H$ [4:2:1]. [207°]. From $C_6H_4Cl(ONa)$ [1.3] by treatment with CO_2 and heating the product, $C_6H_4Cl(O.CO_2Na)$ at 150° (Varnholt, *J. pr.* [2] 36, 28). Also from $C_6H_3(CO_2H)(NO_2)Cl$ [1:2:4] by reduction, diazotisation, and boiling with water. Small needles, volatile with steam, may be sublimed. V. sol. alcohol and chloroform, sl. sol. water. Fe_2Cl_6 gives a violet colour.

Chloro-*p*-oxy-benzoic acid $C_6H_3Cl(OH)CO_2H$ [3:4:1]. [188°] (P.); [170°] (L.). S. ·37 at c. 15°.

Formation.—1. From silver *p*-oxy-benzoate and Cl (Peltzer, *A.* 146, 284; *Z.* [2] 5, 225).—2. From *p*-oxy-benzoic acid and $SbCl_5$ (Lössner, *J. pr.* [2] 13, 432).—3. From *o*-chlorophenol, KOH, CCl_4 and alcohol at 130° (Hasse, *B.* **10, 2192**).

Properties.—Silky needles; v. sol. hot water, v. e. sol. alcohol and ether. May be sublimed. Fe_2Cl_6 gives a reddish-brown pp. in neutral solutions.

Salt.—BaA'$_2$ 6aq.

Methyl derivative $C_6H_3Cl(OMe).CO_2H$. *Chloro-anisic acid.* [215°]. White glistening scales. Formed by oxidation of the methyl-ether of chloro-*p*-cresol.—A'Ag: sparingly soluble pointed plates.—A'$_2$Ba 3½aq: thin rectangular tables, soluble in hot water (Schall a. Dralle, *B.* 17, 2529).

Chloro-*p*-oxy-benzoic acid. ***Methyl derivative*** $C_6H_3Cl(OMe)CO_2H$. *Chloro-anisic acid.* [176°] (C.); [180°] (L.). From anisic acid and Cl (Laurent, *B. J.* 23, 421; Cahours, *A.* 56, 312). Prisms or needles. May be sublimed. Insol. water, v. sol. alcohol and ether. Probably identical with the preceding.

Di-chloro-*o*-oxy-benzoic acid $C_6H_2Cl_2(OH)(CO_2H)$. *Di-chloro-salicylic acid.* [214°]. Prepared by leading Cl into an acetic acid solution of salicylic acid (Smith, *B.* 11, 1225; *A. Ph. S.* 17, 486; *cf.* Cahours, *A. Ch.* [3] 13, 106). Formed also by heating salicylic acid (1 mol.) with $SbCl_5$ (3½ mols.) (Lössner, *J. pr.* [2] 13, 429). Small prisms (from dilute alcohol). Sl. sol. hot water. May be sublimed.

Salts.—A'$_2$Ba 3aq. Long needles, insol. cold water.—A'K: soluble needles.—A'Na: large soluble needles.—A'$_2$Mg: small soluble crystals. A'$_2$Pb. Insoluble pp.

Methyl ether: [142°]; needles.

Ethyl ether: [47°]; needles.

Iso-butyl ether: [188°]; small needles.

Amide: [209°]; needles.

Methyl derivative $C_6H_2Cl_2(OMe)CO_2H$ [104°]. From methyl-salicylic acid and Cl (Procter, *J. Ph.* [3] 3, 275; Cahours, *A. Ch.* [3] 10, 343). Needles.

Ethyl derivative $C_6H_2Cl_2(OEt)CO_2H$. Needles (Cahours, *A. Ch.* [3] 27, 461).

Di-chloro-*p*-oxy-benzoic acid $C_6H_2Cl_2(OH).CO_2H$ [156° uncor.]. Formed by oxidation of di-chloro-*p*-cresol with CrO_3 in acetic acid (Claus a. Riemann, *B.* 16, 1600). Sublimable. Long white needles. Sol. alcohol, ether, and hot water, nearly insol. cold water.—A'Na^x: small needles, sol. water and alcohol.

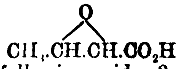
Di-chloro-*p*-oxy-benzoic acid. ***Methyl derivative*** $C_6H_2Cl_2(OMe).CO_2H$. *Di-chloro-anisic acid* [196°]. Formed, together with tetra-chloroquinone, by treating anisic acid with HCl and $KClO_3$ (Reinecke, *Bl.* [2] **7, 177**). Large needles (from alcohol); insol. water.

CHLORO-*o*-OXY-BENZOIC ALDEHYDE $C_7H_5ClO_2$ *i.e.* $C_6H_3Cl(OH).CHO$. From salicylic aldehyde and Cl (Piria, *A.* 30, 169; Löwig, *B. J.* 20, 311). Tables (from alcohol). Insol. water. Combines with $NaHSO_3$ (Bertagnini, *A.* 85, 196). $Ba(O.C_6H_3Cl.CHO)_2$: powder. With NH_3 it forms yellow needles of $(C_6H_3Cl(OH).CH)_3N_2$ (Piria, *A. Ch.* [2] 69, 309).

Chloro-*p*-oxy-benzoic aldehyde $C_6H_3Cl(OH).CHO$. [149°]. From *p*-oxy-benzoic aldehyde and dry chlorine (Herzfeld, *B.* 10, 2196). Silky needles; v. sol. water, alcohol, and ether. Absorbs NH_3 (2 mols.). Fe_2Cl_6 gives a violet colour.

CHLORO-OXY-BENZYL ALCOHOL $C_7H_7ClO_2$ *i.e.* $C_6H_3Cl(OH).CH_2OH$, *Chloro-saligenin.* From chloro-salicin by hydrolysis by emulsin (Piria, *A.* 56, 60). Trimetric plates (from water). Turned blue by Fe_2Cl_6.

***a*-CHLORO-*β*-OXY-BUTYRIC ACID** $CH_3.CH(OH).CHCl.CO_2H$. [63°]. Prepared by addition of hypochlorous acid (ClOH) to (*a*)-crotonic acid (Melikoff, *B.* 16, 1270; *Bl.* [2] 41, 311; 47, 167; Pavoloff, *Bl.* [2] **43, 115**). Needles. V. sol. water.

Reactions.—1. By the action of alcoholic KOH it gives propylene-oxide-carboxylic ((*β*)-methyl-glycidic) acid  $CH_3.\overbrace{CH.CH}^{O}.CO_2H$ [84°] whence HCl forms the following acid.—2. Heating with H_2SO_4 gives *a*-chloro-crotonic acid whence zinc and H_2SO_4 produce crotonic acid.—3. Heating with HCl gives $CH_3.CHCl.CHCl.CO_2H$ [69°] (?) whence alcoholic KOH gives rise to $CH_3.CH{:}CCl.CO_2H$ [98°].

Salts.—A'$_2$Zn: extremely soluble tables.—A'$_2$Ca: easily soluble amorphous powder.

Chloro-oxy-butyric acid $C_3H_5Cl(OH).CO_2H$. [82°].

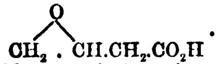
Formation.—1. By the addition of hypochlorous acid (ClOH) to iso-crotonic acid. 2. By the addition of HCl to propylene oxide carboxylic acid.

Properties.—Long prisms. V. sol. water, alcohol and ether. By the action of alcoholic KOH it gives butyro-glycidic acid.

Salts.—A'$_2$Ca 2aq: easily soluble microscopic crystals.—A'$_2$Zn 2aq: trimetric crystals, sl. sol. cold water (Melikoff, *B.* 16, 1268).

Chloro-oxy-butyric acid $CH_2Cl.CH(OH).CH_2.CO_2H$. Formed at the same time as the preceding by the union of HOCl with isocrotonic acid (Melikoff, *J. R.* 16, 541).

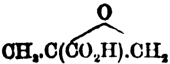
Liquid. Converted by alcoholic KOH into propylene oxide carboxylic ((γ)-methyl-glycidic) acid



$\overset{O}{\widehat{CH_2\,.\,CH}}.CH_2.CO_2H$.

Chloro-oxy-isobutyric acid $CH_2Cl.CMe(OH).CO_2H$. *Chloro-acetonic acid.* [107°]. (c. 233°).

Formation.—1. From chloro-acetone by treatment with HCN and saponification of the resulting nitrile (Bischoff, *B.* 5, 865).—2. From methacrylic acid and HOCl (Melikoff, *Bl.* [2] 41, 311; 43, 116).—3. From propylene oxide carboxylic acid ((α)-methyl-glycidic acid)



$CH_2.\overset{O}{\widehat{C(CO_2H).CH_2}}$ and conc. HCl (M.).

Properties.—Long prisms (from ether); v. sol. water. Converted by alcoholic KOH into propylene-oxide carboxylic acid.

Salts.—CaA'_2 2aq. ZnA'_2.

Nitrile $CH_2Cl.CMe(OH).CN$. From chloro-acetone, by boiling with alcohol and conc. aqueous HCN (B.). Oil. Split up by distillation into HCy and $C_4H_4Cl_2O$.

Chloro-oxy-butyric acid. ***Nitrile*** $C_4H_6ClNO_4$. From epichlorhydrin and anhydrous HCy at 140° (Hörmann, *B.* 12, 23). Liquid, v. sol. water. Dilute HCl forms a liquid chloro-oxy-butyric acid.

Di-chloro-oxy-isobutyric acid $CHCl_2.CMe(OH).CO_2H$. [83°]. From its nitrile and HClAq at 100° (Bischoff, *B.* 8, 1334). Prisms.—AgA'.

Ethyl ether EtA'. (c. 212°).

Nitrile $CHCl_2.CMe(OH).CN$. From di-chloro-acetone and conc. aqueous HCy (B.). Liquid. Split up by distillation or by alkalis into HCy and di-chloro-acetone. Aqueous KCy forms crystalline $(C_3H_4Cl_2O)_2HCN$ (Glutz a. Fischer, *J. pr.* [2] 4, 52).

Di-chloro-oxy-isobutyric acid $(CH_2Cl)_2C(OH).CO_2H$. [92°]. Obtained by boiling its nitrile for 12 hours with conc. HClAq (Grimaux a. Adam, *Bl.* [2] 36, 20). Deliquescent tables, v. sol. alcohol and ether. KCN converts it into a nitrile of citric acid $(CH_2CN)_2C(OH).CO_2H$.

Ethyl ether EtA'. (c. 228°). From *s*-di-chlorhydrin, chloroformic ether, and sodium amalgam (Kelly, *B.* 11, 2222). Conc. KOH produces glycerin.

Nitrile $(CH_2Cl)_2C(OH).CN$. From *s*-di-chloro-acetone (50 g.) by digesting with HCy (20 g.), a little water, and alcohol 8 c.c.

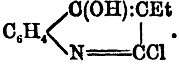
Tri-chloro-oxy-isobutyric acid $CCl_3.CMe(OH).CO_2H$. From tri-chloro-acetone by successive treatment with HCy and HCl (Bischoff, *B.* 8, 1339). Syrup.

TRI-CHLORO-DI-OXY-DI-CYMYL-ETHANE $C_{22}H_{27}Cl_3O_2$ *i.e.* $CCl_3.CH(C_{10}H_{12}OH)_2$. [194°]. From thymol (2 mol.), chloral (1 mol.) and conc. H_2SO_4 diluted with HOAc (Jaeger, *B.* 7, 1197; *C. J.* 31, 262). Monoclinic needles (containing HOEt). Insol. water. Alcohol and zinc-dust form $CH_3CH(C_{10}H_{12}OH)_2$ and $CH_2:C(C_{10}H_{12}OH)_2$.

CHLORO-OXY-ETHYL-AMIDO-PHENYL-ETHANE $CCl_3.CH(OH).C_6H_4NHEt$. [98°]. From chloral hydrate and ethyl-aniline (Boessneck, *B.* 21, 782).

Nitrosamine $C_{10}H_{11}Cl_3N(NO)$ [138°].

(*Py.* 3:1:2)-**CHLORO-OXY-ETHYL-QUINOLINE**



$C_6H_4\left<\begin{matrix}C(OH):CEt\\ \qquad|\\ N{=\!=}CCl\end{matrix}\right.$. [248°]. Formed by the action of PCl_5 upon aniline ethyl-malonate under benzene. Colourless needles. M. sol. alcohol (Kiliani, *B.* 20, 1235).

TRI-CHLORO-OXY-ETHYL-SUCCINIC ACID ***Lactone.*** $CCl_3.\underbrace{CH.CH(CO_2H).CH_2.CO.O}$. *Tri-chloro-methyl-paraconic acid.* [97°]. From chloral, sodium succinate and Ac_2O (Fittig, *B.* 20, 3179). Converted by baryta into barium isocitrate.

DI-CHLORO-DI-OXY-HEXANE $C_6H_{12}Cl_2O_2$ *i.e.* $CH_2Cl.CH(OH).CH_2.CH_2.CH(OH).CH_2Cl$. (?) S.G. ^{7} 1·4. From diallyl and aqueous HOCl in the cold (Henry, *B.* 7, 415; *Z.* [2] 5, 479). Oil. Potash converts it into diallyl dioxide whence baryta-water produces the anhydride of tetra-oxy-hexane $C_6H_{12}O_4$ (Przibytek, *Bl.* [2] 45, 248).

Di-chloro-tetra-oxy-hexane *v.* MANNITE.

DI-CHLORO-DI-OXY-HEXINOIC ACID $C_6H_6Cl_2O_4$ *i.e.* $CH_2Cl.C(OH):CCl.C(OH):CH.CO_2H$ (?). *Di-chloro-di-oxy-amenyl carboxylic acid.* [177°]. From the following by sodium amalgam (Hantzsch, *B.* 20, 2789). Lustrous prisms. Conc. aqueous NaOH forms $C_6H_4ClO_4Na_2$ 6aq which crystallises in canary yellow needles and is converted by HCl into $C_6H_5ClO_2$ [97°], which forms a salt NaA' 3aq.—NH_4A'. [185°].

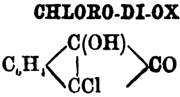
Acetyl derivative [134°].

Tri-chloro-di-oxy-hexinoic acid $C_6H_5Cl_3O_4$ *i.e.* $CH_2Cl.C(OH):CCl.C(OH):CCl.CO_2H$ (?) [177°]. Formed, together with tri-chloro-phenol, by passing chlorine into an alkaline solution of phenol (Hantzsch, *B.* 20, 2789). The yield is 50 p.c. Needles (from water); or monoclinic crystals (containing 4aq). Decomposed by conc. aqueous KOH.—NH_4A' 2aq: trimetric prisms, sl. sol. water.

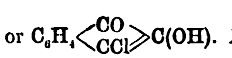
Methyl ether MeA'. [126°].

Di-acetyl derivative $C_6H_3Ac_2Cl_3O_4$. [188°–192°].

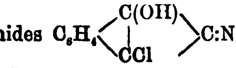
CHLORO-DI-OXY-INDONAPHTHENE



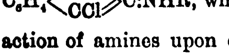
$C_6H_4\left<\begin{matrix}C(OH)\\|\\CCl\end{matrix}\right>CO$ or



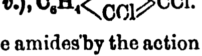
$C_6H_4\left<\begin{matrix}CO\\CCl\end{matrix}\right>C(OH)$. *Phenylene-chloro-oxy-acetylene-ketone.* [114°]. Formed by the action of acids or alkalis upon the amides



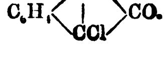
$C_6H_4\left<\begin{matrix}C(OH)\\|\\CCl\end{matrix}\right>C:NR$ or



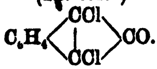
$C_6H_4\left<\begin{matrix}CO\\CCl\end{matrix}\right>C:NHR$, which are obtained by the action of amines upon di-chloro-oxy-indonaphthene (*q.v.*),

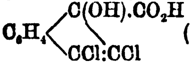


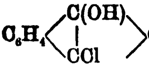
$C_6H_4\left<\begin{matrix}CO\\CCl\end{matrix}\right>CCl$. It is reconverted into these amides by the action of amines (Zincke, *B.* 20, 1271). White glistening plates (from dilute alcohol), or small compact crystals (from petroleum-spirit). Dissolves in aqueous alkalis with a red colour. By PCl_5 it is converted into the compound



$C_6H_4\left<\begin{matrix}CCl\\|\\CCl\end{matrix}\right>CO$.

(In. 3:1:2)-Di-chloro-oxy-indonaphthene  [125°]. Formed by the action of PCl_5 upon chloro-di-oxy-indonaphthene $C_6H_4\left<\begin{matrix}C(OH)\\CCl\end{matrix}\right>CO$. Glistening plates (from dilute alcohol) (Zincke, *B.* 20, 1272).

(*In.* 3:2:1)-Di-chloro-oxy-indonaphthene $C_6H_4\left<\begin{matrix}CO\\CCl\end{matrix}\right>CCl$. *Phenylene-di-chloro-acetylene-ketone.* [90°]. Formed by oxidation of the carboxylic acid  (from di-chloro-(β)-naphthoquinone) with CrO_3. Small yellow or long glistening golden needles. Very volatile with steam. It has some of the characteristics of a quinone. With aromatic bases it forms coloured compounds. Reacts with hydroxylamine and with phenylhydrazine. With halogens it yields colourless addition-products. It is not affected by $SnCl_2$ or by PCl_5.

Methyl-amide $C_6H_4\left<\begin{matrix}CO\\CCl\end{matrix}\right>C.NHMe$ or  : [195°]; long dark-red needles, sol. hot alcohol and acetic acid, sl. sol. benzene.

Di-methyl-amide $C_6H_4{:}C_3ClO.NMe_2$: [140°]; long red needles or thick tables.—$B'_2H_2Cl_2PtCl_4$: yellow crystalline pp.

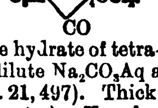
Anilide $C_6H_4{:}C_3ClO.NHPh$: [204°]; slender deep-red needles; dissolved in warm dilute alkalis without decomposition.

Oxim $C_6H_4\left<\begin{matrix}C(NOH)\\CCl\end{matrix}\right>CCl$: [120°]; long yellow needles; v. sol. warm alcohol and acetic acid (Zincke, *B.* 20, 1265).

Di-chloride $C_6H_4\left<\begin{matrix}CO\\CCl_2\end{matrix}\right>CCl_2$. [108°]. Converted by aqueous NaOH into tri-chloro-vinyl-benzoic acid [163°] (Zincke a Fröhlich, *B.* 20, 2053).

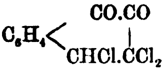
Di-bromide $C_6H_4\left<\begin{matrix}CO\\CClBr\end{matrix}\right>CClBr$. [114°], and, when rapidly heated, [c. 128°]. Converted by aqueous NaOH into di-chloro-bromo-vinyl-benzoic acid $CClBr{:}CCl.C_6H_4.CO_2H$ [174°].

Chloro-oxy-indonaphthalene dichloride $C_6H_4\left<\begin{matrix}CO\\CHCl\end{matrix}\right>CCl_2$. [59°]. From the dihydride of tri-chloro-di-oxy-indonaphthene carboxylic acid and dilute CrO_3Aq (Zincke, *B.* 20, 2890). Thick needles (from alcohol). Converted by alkalis into di-chloro-vinyl-benzoic acid.

DI-CHLORO-DI-OXY-INDONAPHTHENE CARBOXYLIC ACID  [139°]. Formed by dissolving the hydrate of tetra-chloro-(β)-naphthoquinone in dilute Na_2CO_3Aq and ppg. with an acid (Zincke, *B.* 21, 497). Thick needles (containing aq) (from water). V. sol. alcohol, benzene, and HOAc. CrO_3 gives $C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>CCl_2$ [124°].

Methyl ether MeA′ [124°] large oblique crystals.

Acetyl derivative $C_{10}H_5AcCl_2O_4$. [126°]. Prisms.

Tri-chloro-oxy-indonaphthene carboxylic acid. *Dihydride* $C_{10}H_7Cl_3O_3$ *i.e.* $C_6H_4\left<\begin{matrix}C(OH).CO_2H\\CHCl\end{matrix}\right>CCl_2$. From the dihydride of di-chloro-(β)-naphthoquinone  and dilute NaOH (Zincke a. Fröhlich, *B.* 20, 2894). Liquid.

Methyl ether MeA′. [150°].

Acetyl derivative of the methyl ether $C_{10}H_5MeAcCl_2O_3$. [116°].

DI-CHLORO-OXY-METHANE SULPHINIC ACID $CCl_2(OH)SO_2H$. Unstable deliquescent needles.

Salt.—A′K. Trimetric plates. From KCy and aqueous or alcoholic trichloro-methane sulphochloride (*q.v.*): $CCl_3.SO_2Cl + KCy + H_2O = CyCl + HCl + CCl_2(OH).SO_2K$. Boiled with potash it forms KCl and K_2SO_4 (Loew, *Z.* 1868, 518; McGowan, *J. pr.* [2] 30, 288).

DI-CHLORO-OXY-METHANE SULPHONIC ACID.

Chloride.—$CCl_2(OH)SO_2Cl$. From PCl_5 and $CCl_2(OH)SO_2K$ (McGowan, *J. pr.* [2] 30, 289).

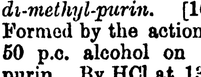
Anilide.—$CCl_2(OH)SO_2NPhH$. Rhombohedra. From aniline and the above chloride.

TRI-ω-CHLORO-α-OXY-METHYL-AMIDO-PHENYL-ETHANE $CCl_3.CH(OH)C_6H_4NHMe$. [112°]. From chloral hydrate and methyl-aniline (Boessneck, *B.* 21, 782).

Nitrosamine $CCl_3.CH(OH).C_6H_4NMeNO$. [118°]. Needles.

Tri-α-chloro-α-oxy-di-methyl-amido-benzene $CCl_3.CH(OH).C_6H_4NMe_2$. Formed by condensation of chloral hydrate with di-methyl-aniline in presence of $ZnCl_2$ (Knöfler a. Boessneck, *B.* 20, 3193).

(*Py.* 3:1)-CHLORO-OXY-(*B.* 4)-METHYL-(*Py.* 2)-ETHYL-QUINOLINE

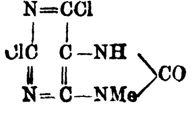


α-Chloro-β-ethyl-γ-oxy-o-toluquinoline. [225°]. Formed by the action of PCl_5 upon σ-toluidine ethyl-malonate under benzene. Silky needles (from alcohol) (Kiliani, *B.* 20, 1233).

CHLORO-DI-OXY-METHYL-PURIN.

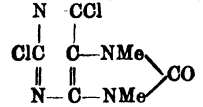
Methyl ethyl derivative $C_5N_4(CH_3)(OMe)(OEt)Cl$ (?) *Ethoxy-chloro-oxy-di-methyl-purin.* [160°]. Granular crystals. Formed by the action of a solution of NaOH in 50 p.c. alcohol on di-chloro-methoxy-methyl-purin. By HCl at 130° it is converted into tri-oxy-di-methyl-purin (di-methyl-uric acid). By HI it is reduced to di-oxy-di-methyl-purin (Fischer, *B.* 17, 335).

Di-ethyl derivative $C_5(CH_3)(OEt)_2ClN_4$. Formed by heating tri-chloro-methyl-purin with alcoholic NaOH (Fischer, *B.* 17, 332). Fine felted needles. Heated with HCl at 130° it gives methyl-uric acid (tri-oxy-methyl-purin).

Di-chloro-oxy-methyl-purin $C_6H_4ON_4Cl_2$ *i.e.* $C_5(CH_3)(OH)Cl_2N_4$ probably 

[274°]. Obtained by heating methyl-uric acid with PCl_5 and $POCl_3$ at 130° (Fischer, *B.* **17**, 330, 1786). Fine white needles. Very stable body, volatilising without decomposition and not being attacked by HNO_3 or by $KClO_3$ and HCl. By HI it is reduced to oxy-methyl-purin.

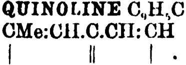
Di-chloro-oxy-di-methyl-purin $C_7H_6OCl_2N_4$ *i.e.*



$$\begin{array}{lll} N & \text{—CCl} & \\ | & | & \\ ClC & C\text{—NMe} & \\ \| & \| & \rangle CO \\ N\text{—} & C\text{—NMe} & \end{array}$$

or $C_5N_4(CH_3)(OMe)Cl_2$ [183°]. *Di-chloro-methoxy-methyl-purin.* Formed by heating the lead compound of di-chloro-oxy-methyl-purin with methyl iodide (Fischer, *B.* 17, 334, 1787). Fine colourless needles. Insol. alkalis. By HI it is reduced to methoxy-methyl-purin.

(*Py.* 4, 3) - **CHLORO-OXY** - (*B.* 2) - **METHYL-QUINOLINE** $C_9H_5CH_3NOCl$ *i.e.*

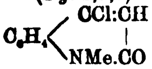


$$\begin{array}{l} CMe{:}CH.C.CH{:}CH \\ |\qquad\quad \|\quad\ \ | \\ CH{:}CH.C{:}NCl.CO \end{array}$$

. *Chloro-methyl-pseudocarbostyril.* [121°]. Formed by treating a solution of (*B.* 2) methylquinoline in boric acid with bleaching powder solution (Einhorn a. Lauch, *A.* 243, 358). White needles (from acetic ether).

Reactions.—1. Boiled with NaOHAq (*B.* 2)-methyl-carbostyril [228°] is obtained.—2. Yields an isomeride [281°] on boiling with alcohol.

(*Py.* **1,3,4)-Chloro-oxy-methyl-quinoline**

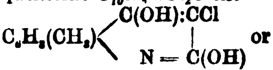


$$C_6H_4\left\langle\begin{array}{l} CCl{:}CH \\ \qquad\ \ | \\ NMe.CO \end{array}\right.$$

[117·5°]. From (γ)-chloro-carbostyril, MeI, and alcoholic NaOH (Friedländer a. Muller, *B.* **20**, 2009). Hair-like needles (from MeOH).

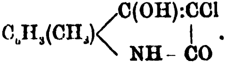
(*Py.*)-**Chloro-di-oxy**-(*B.* 2)-methyl-quinoline *Di-ethyl derivative* $C_6H_3(CH_3)NC_3Cl(OEt)_2$. [71°]. Formed by heating (*Py.* 1:2:3)-tri-chloro-(*B.* 2)-methyl-quinoline with a solution of sodium in absolute alcohol at 100°-130°. Long colourless needles (Rugheimer a. Hoffmann, *B.* 18, 2982).

(*Py.* **2:3:1**) - **Chloro - di - oxy**-(*B.* 4) - **methyl - quinoline** $C_{10}H_7NCl_2O$ *i.e.*



$$C_6H_3(CH_3)\left\langle\begin{array}{l} C(OH){:}CCl \\ \qquad\quad | \\ N = C(OH) \end{array}\right.$$

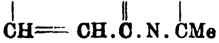
or



$$C_6H_3(CH_3)\left\langle\begin{array}{l} C(OH){:}CCl \\ \qquad\quad | \\ NH - CO \end{array}\right.$$

. *Chloro-oxy-tolucarbostyril.* [277°]. Formed by heating (*Py.* 2:3:1)-di-chloro-oxy-(*B.* 4)-methyl-quinoline with dilute HCl at 160°. Large plates or tables. V. sol. acetic acid, sl. sol. alcohol, insol. water. Dissolves in acids and alkalis (Rugheimer a. Hoffmann, *B.* 18, 2986).

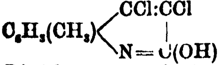
(*Py.* **1)-Chloro-**(*B.* **2)-oxy-methyl-quinoline.** ***Methyl derivative***



$$\begin{array}{l} C(OMe){:}CH.C.CCl.CH \\ |\qquad\qquad\quad \|\qquad | \\ CH{=\!=}\ CH.C.N.CMe \end{array}$$

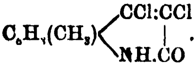
[100°]. (c. 298°). From the corresponding $C_9H_4Me(OH)(OMe)N$ by $POCl_3$ (Conrad a. Limpach, *B.* 21, 1649). Silky prisms.

(*Py.* **1:2:3) - Di - chloro - oxy** - (*B.* **2) - methyl - quinoline** $C_{10}H_7NCl_2O$ *i.e.*



$$C_6H_3(CH_3)\left\langle\begin{array}{l} CCl{:}CCl \\ \qquad\ | \\ N = C(OH) \end{array}\right.$$

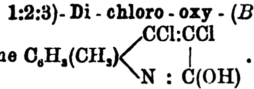
or



$$C_6H_3(CH_3)\left\langle\begin{array}{l} CCl{:}CCl \\ \qquad\ \ | \\ NH.CO \end{array}\right.$$

. *Di-chloro-tolucarbostyril.* [292°]. Obtained by heating (*Py.* 1:2:3)-tri-chloro-(*B.* 2)-methyl-quinoline with dilute HCl at 180°. Small crystals. Sol. benzene and acetic acid, sl. sol. alcohol and ether, insol. water. Has both weak basic and weak acid properties (Rugheimer a. Hoffmann, *B.* 18, 2981).

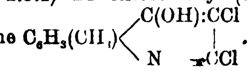
(*Py.* **1:2:3)- Di - chloro - oxy** - (*B.* **4) - methyl - quinoline**



$$C_6H_3(CH_3)\left\langle\begin{array}{l} CCl{:}CCl \\ \qquad\ | \\ N : C(OH) \end{array}\right.$$

. *Di-chloro-tolucarbostyril.* [288°]. Formed by heating (*Py.* 1:2:3)-tri-chloro-(*B.* 4)-methyl-quinoline with dilute HCl at 180°. Small white needles (from acetic acid). Sublimes in needles. Sl. sol. alcohol, insol. water (Rugheimer a. Hoffmann, *B.* 18, 2985).

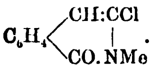
(*Py.* 2:3:1) - **Di - chloro - oxy** - (*B.* 4) - **methyl-quinoline**



$$C_6H_3(CH_3)\left\langle\begin{array}{l} C(OH){:}CCl \\ \qquad\qquad | \\ N \quad\ \ CCl \end{array}\right.$$

. [245°]. Formed by the action of PCl_5 upon the acid malonate of *o*-toluidine in presence of cold benzene. Needles. Sl. sol. alcohol and acetic acid, nearly insol. water. Decomposes alkaline carbonates (Rugheimer a. Hoffmann, *B.* 18, 2983).

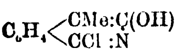
(*Py.* **2 : 4 : 3) - CHLORO-OXY-METHYL-ISO-QUINOLINE** $C_{10}H_8ClNO$ *i.e.*



$$C_6H_4\left\langle\begin{array}{l} CH{:}CCl \\ \qquad\ \ | \\ CO.NMe \end{array}\right.$$

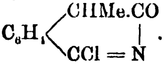
. [112°]. Formed by methylation of (*Py.* 2:4)-chloro-oxy-isoquinoline [220°]. Long needles. V. sol. ether, benzene, chloroform, and hot alcohol (Gabriel, *B* 19, 2361).

(*Py.* 4:2:1)-**Chloro-oxy-methyl-isoquinoline**



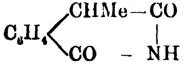
$$C_6H_4\left\langle\begin{array}{l} CMe{:}C(OH) \\ CCl\ {:}N \end{array}\right.$$

or



$$C_6H_4\left\langle\begin{array}{l} CHMe.CO \\ \qquad\quad | \\ CCl = N \end{array}\right.$$

. [224°]. Needles (from acetic acid). Sol. aqueous alkalis. Formed as a by-product of the reaction of $POCl_3$ upon the imide of phenyl-methyl-acetic-*o*-carboxylic acid



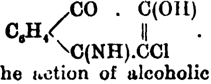
$$C_6H_4\left\langle\begin{array}{l} CHMe - CO \\ \qquad\quad\ | \\ CO\ \ -\ NH \end{array}\right.$$

(Gabriel, *B.* 20, 2501).

CHLORO-OXY-(α)-**NAPHTHOQUINONE** $C_{10}H_5ClO_2$ *i.e.* $C_{10}H_4Cl(OH)O_2$. *Chloro-naphthalic acid.* [above 200°]. Formed by boiling chloro-naphthalene tetrachloride with HNO_3 (Laurent, *A.* 35, 293). Formed also by boiling di-chloro-naphthoquinone with alcoholic KOH (Graebe, *A.* 149, 14; P. a. E. Depouilly, *Bl.* [2] 4, 10); and by boiling the alkylamides of chloro-(α)-naphthoquinone with acids or aqueous KOH. Yellow needles; may be sublimed. Insol. water, m. sol. alcohol and ether. HNO_3 oxidises it to phthalic and oxalic acids. Turned red by alkalis. Distillation with PCl_5 gives penta-chloro-naphthalene.

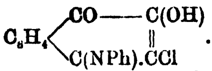
Salts. $KC_{10}H_4ClO_4$ *x*aq: crimson needles.—BaA'_2 aq: silky orange needles.

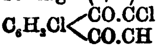
Imide



$$C_6H_4\left\langle\begin{array}{l} CO\ \ .\ \ C(OH) \\ \qquad\qquad \| \\ C(NH).CCl \end{array}\right.$$

. [c. 260°]. Formed by the action of alcoholic NH_3 upon a hot alcoholic solution of chloro-(β)-naphthoquinone. Dark metallic plates. Sl. sol. alcohol and acetic acid. Dissolves in dilute NaOH with a dark-violet colour. Long boiling with HCl yields chloro-oxy-(α)-naphthoquinone (Zincke, *B.* **19**, 2499).

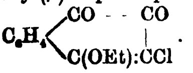
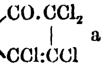
Anilide 
$C_6H_4\left\langle\begin{array}{l}CO\text{——}C(OH)\\ \qquad\quad\ \|\\ C(NPh).CCl\end{array}\right.$. [253°]. Dark metallic plates. Formed by the action of aniline upon a hot alcoholic solution of chloro-(β)-naphthoquinone (Zincke, *B.* 19, 2499).

(‘β’)-Chloro-oxy-(α)-naphthoquinone $C_{10}H_4Cl(OH)O_2$. [205° uncor.]. Formed by boiling (‘β’)-di-chloro-(α)-naphthoquinone  $C_6H_2Cl\left\langle\begin{array}{l}CO.CCl\\ CO.CH\end{array}\right.$ with alkalis. Felted yellow needles. V. sol. alcohol, ether, &c., sl. sol. water. Sublimable. The alkali-salts are v. sol. water with a deep red colour; the Ca and Ba salts are sparingly soluble.—A'_2Cu: insoluble red pp.—A'_2Pb: yellowish red pp.

Anilide $C_{10}H_4Cl(NHPh)O_2$: [155° uncor.]. Formed by boiling an alcoholic solution of (‘β’)-di-chloro-naphthoquinone with aniline. Dark violet crystals. V. sol. acetic acid, sl. sol. alcohol.

o-Toluide $C_{10}H_4Cl(NHC_7H_7)O$: [175° uncor.].

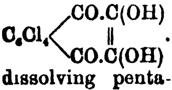
p-Toluide $C_{10}H_4Cl(NHC_7H_7)O_2$: [164° uncor.] (Claus a. Müller, *B.* 18, 3074).

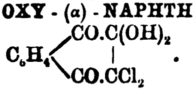
Chloro-oxy-(β)-naphthoquinone. *Ethyl derivative*  $C_6H_4\left\langle\begin{array}{l}CO\ \text{- -}\ CO\\ \qquad\quad\ |\\ C(OEt):CCl\end{array}\right.$. [149°]. From tetra-chloro-(α)-naphthol  $C_6H_4\left\langle\begin{array}{l}CO.CCl_2\\ \qquad\ |\\ CCl:CCl\end{array}\right.$ and alcoholic KOH (Zincke, *B.* 21, 1027). Orange needles.

Propyl derivative $C_{10}H_4ClO_2(OPr)$. [190°]. Formed in like manner, using propyl alcohol.

Tri-chloro-oxy-(α)-naphthoquinone $C_{10}H_2Cl_3(OH)O_2$. [235° uncor.]. Formed by boiling tetra-chloro-(α)-naphthoquinone with alcoholic KOH. Yellow needles. Sublimable. V. sol. alcohol, ether, &c., sl. sol. water. Its salts are deep red. By treatment with aniline it gives an anilide [180° uncor.], which forms coppery needles. Sol. hot alcohol, acetic acid, and ether, sl. sol. cold alcohol, insol. water.

The corresponding *o*- and *p*-toluidine derivatives melt at [205°] and [203°] uncor. respectively (Claus, *B.* 19, 1141).

Tetra-chloro-oxy-(α)-naphthoquinone 
$C_6Cl_4\left\langle\begin{array}{l}CO.C(OH)\\ \qquad\ \|\\ CO.C(OH)\end{array}\right.$. [265° uncor.]. Formed by dissolving penta-chloro-(α)-naphthoquinone in alcoholic KOH, and precipitating the acid by HCl. Sublimes in yellow needles. The alkaline salts are v. sol. water, the Ag, Pb, Cu, &c. salts are red pps. (Claus a. Wenzlik, *B.* 19, 1168).

DI-CHLORO-DI-OXY-(α)-NAPHTHOQUINONE DIHYDRIDE  $C_6H_4\left\langle\begin{array}{l}CO.C(OH)_2\\ \qquad\ |\\ CO.CCl_2\end{array}\right.$. [105°]. From chloro-amido-naphthoquinone and Cl (Zincke a. Gerland, *B.* 20, 3216). Thick needles. Converted by alkalis into compound [129°] which may be oxidised to another [125°].

CHLORO-OXY-NAPHTHOQUINONE SULPHONIC ACID (?) $C_{10}H_5ClSO_6$ *i.e.* $C_{10}H_3ClO_2(OH)(SO_3H)$. From naphthalene, $KClO_3$, and H_2SO_4 (Hermann, *A.* 151, 63; *Z.* [2] 4, 551). Amorphous mass, m. sol. water, v. sol. alcohol and ether. When boiled with water it exchanges Cl for OH. The K salt is a red dye.

(2, 8 ?)-Chloro-oxy-(α)-naphthoquinone (3′)-sulphonic acid $C_{10}H_4ClO_2(OH)(SO_3H)$. [211°]. From di-chloro-naphthoquinone sulphonic acid by displacing Cl by OH (Claus, *J. pr.* [2] 37, 184). Crystals; v. sol. water, sl. sol. alcohol, insol. ether.

Salts.—The normal salts are yellowish-red, the basic salts are dark red.—Na_2A'' 2aq.—BaA'' 2aq. PbA''.—Ag_2A''aq.

Phenyl derivative $C_{10}H_3(SO_3H)Cl(OPh)O_2$. [121°]. Formed by the addition of phenol and a small quantity of potash to a hot solution of the sodium salt. $C_{10}H_3(SO_3Na)Cl(OPh)O_2(PhOH)$.—$BaA'_2$2PhOH. Small needles (from water).—AgA′PhOH. Needles. V. sol. hot, sl. sol. cold, water.

Acetyl derivative $C_{10}H_3(SO_3H)Cl(OAc)O_2$. Salts.—NaA′: bright yellow needles. The Ag, Pb and Ba salts form double salts with the precipitant.

CHLORO-OXY-NICOTINIC ACID *v.* CHLORO-OXY-PYRIDINE CARBOXYLIC ACID.

DI-CHLORO-DI-OXY OCTANE $C_8H_{14}Cl_2(OH)_2$. Formed by the action of ClOH on CH_2:CMe.CH_2.CH_2.CMe:CH_2 (Przybitek, *B.* 20, 3239).

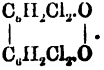
DI-CHLORO-OXY-OCTOIC ACID $C_8H_{14}Cl_2O_3$ *i.e.* $(C_3H_6Cl)_2C(OH).CO_2H$. Formed by the union of HCl with $(C_3H_5)_2C(OH).CO_2H$ obtained from oxalic ether and zinc allyl (Schatzky, *J. R.* 17, 73). Syrup.

DI-CHLORO-HEXA-OXY-DIPHENYL.

Tetra-methyl ether. $C_{16}H_{16}Cl_2O_6$ ***i.e.*** $C_{12}H_2Cl_2(OH)_2(OMe)_4$. *Di-chloro hydrocœrulignon.* [220°]. From its acetyl derivative and alcoholic KOH (Hayduck, *B.* 9, 929). Small plates (from alcohol). M. sol. hot alcohol.—$C_{16}H_{14}K_2Cl_2O_6$: needles. BaA″.

Di-acetyl-derivative $C_{12}H_2Cl_2(OAc)_2(OMe)_4$. [172°]. From di acetyl-cœrulignon and PCl_5. Small prisms.

Hexa-methyl ether $C_{12}H_2Cl_2(OMe)_6$. From $C_{12}H_4(OMe)_6$ and Cl (Ewald, *B.* 11, 1624). Needles (from alcohol).

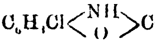
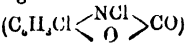
Tetra-chloro-di-oxy-diphenyl $C_{12}H_6Cl_4O_2$ ***i.e.*** $C_6H_2Cl_2(OH).C_6H_2Cl_2(OH)$. [233° uncor.]. From di-oxy-diphenyl in HOAc and Cl (Magatti, *B* 13, 227). Needles (from dilute alcohol). Fuming HNO_3 gives dark red insoluble scales of 
$\begin{array}{l}C_6H_2Cl_2.O\\ |\qquad\quad\ |\\ C_6H_2Cl_2O\end{array}$.

Octo-chloro-di-oxy-diphenyl $C_{12}Cl_8(OH)_2$. *Per-chloro-diphenol.* [234°]. Prepared by heating per-chloro-diphenyl with alcoholic NaOH at 150° (Weber a. Söllscher, *B.* 16, 883). Quadratic tables. Sol. benzene and alkalis.

Di-methyl ether $C_{12}Cl_8(OMe)_2$: [226°]; long white needles.

Di-acetyl derivative $C_{12}Cl_8(OAc)_2$: [194°]; pointed crystals.

CHLORO-OXY-PHENYL-CARBAMIC ACID.

Anhydride  $C_6H_3Cl\left\langle\begin{array}{c}NH\\ O\end{array}\right\rangle CO$. *Carbonyl-chloro amido-phenol.* [193°]. Formed by boiling with alcohol the product  $\left(C_6H_3Cl\left\langle\begin{array}{c}NCl\\ O\end{array}\right\rangle CO\right)$ of the action of bleaching powder on $C_6H_4<\substack{NH\\O}>CO$ (Jacoby, *J. pr.* [2] 37, 32). Plates (from water, HOAc, and benzene). Sl. sol. hot water. May be sublimed.

Eso-ν-di-chloro-oxy-phenyl-carbamic acid. *Anhydride* $C_6H_3Cl<\substack{NCl\\O}>CO$. (*a*)-*Carbonyl chloro-phenol chlorimide.* [119°]. From the preceding and chlorine-water (Jacoby, *J. pr.* [2] 37, 40). Plates; m. sol. chloroform and benzene. Converted by heat into the following isomeride. Converted into the preceding body by boiling with alcohol, ether, water, aniline, di-methyl-aniline, and phenyl-hydrazine.

Di-chloro-oxy-phenyl-carbamic acid. *Anhydride* $C_6H_2Cl_2<\substack{NH\\O}>CO$. (*a*) - *Carbonyl - di - chloro-amido-phenol.* [270°]. The chief product of the action of heat on the preceding, the following isomeride being also formed (*J.*). Prisms (from alcohol). May be sublimed.

Di-chloro-oxy-phenyl-carbamic acid. *Anhydride* $C_6H_2Cl_2<\substack{NH\\O}>CO$. (*β*)-*Carbonyl-di-chloro-amido-phenol.* [214°]. Formed as above. Needles; v. e. sol. alcohol, ether, and HOAc; m. sol. water. Sublimes in needles.

Tri-chloro-oxy-phenyl-carbamic acid. *Anhydride* $C_6H_2Cl_2<\substack{NCl\\O}>CO$. (*a*)-*Carbonyl-di-chloro-phenol chlorimide.* [c. 147°]. From $C_6H_3Cl<\substack{NCl\\O}>CO$ and a solution of bleaching-powder (Jacoby, *J. pr.* [2] 37, 46).

Tri-chloro-oxy-phenyl-carbamic acid. *Anhydride* $C_6H_2Cl_2<\substack{NCl\\O}>CO$. [89°]. (*β*)-*Carbonyl - di - chloro - phenol chlorimide.* From $C_6H_2Cl_2<\substack{NH\\O}>CO$ in HOAc by adding a solution of bleaching-powder (J.). Needles; sol. water.

Tri-chloro-oxy-phenyl-carbamic acid. *Anhydride* $C_6HCl_3<\substack{NH\\O}>CO$. *Carbonyl - tri-chloro-amido-phenol.* [262°]. Formed from $C_6H_4<\substack{NH\\O}>CO$ in HOAc by chlorination and subsequent decomposition of the product by boiling alcohol (J.). Needles, sl. sol. alcohol, HOAc, and water. Sublimes in plates.

Tetra-chloro-oxy-phenyl-carbamic acid. *Anhydride* $C_6Cl_4<\substack{NH\\O}>CO$. *Carbonyl-tetra-chloro-amido-phenol.* [c. 229°]. Formed by heating $C_6HCl_3<\substack{NCl\\O}>CO$ which is obtained by treating a solution of the preceding in HOAc with bleaching-powder (Jacoby, *J. pr.* [2] 37, 48). White crystalline sublimate; sl. sol. water; m. sol. alcohol and HOAc; v. sol. ether and benzene. Converted by bleaching-powder solution into $C_6Cl_4<\substack{NCl\\O}>CO$ whence it is regenerated by boiling with alcohol.

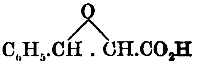
TRI - CHLORO - DI - OXY - DI - PHENYL - ETHANE $C_{14}H_{11}Cl_3O_2$ *i.e.* $CCl_3.CH(C_6H_4OH)_2$. [202°]. From phenol, chloral, H_2SO and HOAc at 0° (ter Meer, *B.* 7, 1201). Small crystals; v. sol. alcohol and ether. Alcohol and zinc-dust give $CH_2:C(C_6H_4OH)_2$.

Di-acetyl derivative $CCl_3.CH(C_6H_4OAc)_2$. [138°]. Needles.

DI - CHLORO - OXY - PHENYL - METHYL - PYRAZOLE $C_{10}H_8N_2OCl_2$ *i.e.* $Ph.N<\substack{CO-CCl_2\\N=CMe}>$. [61°]. Obtained by passing chlorine into oxy-phenyl-methyl-pyrazole dissolved in chloroform (Knorr, *A.* 238, 178). Crystalline mass, volatile with steam, insol. water and alkalis, sol. alcohol and ether. Reduced by Sn and HCl to oxy-phenyl-methyl-pyrazole.

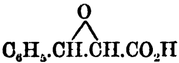
β-CHLORO-(a)-OXY - PHENYL - PROPIONIC ACID $C_9H_9ClO_3$ *i.e.* $Ph.CH(OH).CHCl.CO_2H$ [101°]. From sodic cinnamate, sodic carbonate and chlorine (Glaser, *A.* 147, 80; 219, 183) or better, from potassic cinnamate and HClO (Erlenmeyer a. Lipp, *A* 219, 184). Slender six-sided laminæ (containing aq). Melts, in the hydrated condition, at 80°. M. sol. cold water.

Reactions.—1. *Alkalis* form so-called *β*-oxy-phenyl-cinnamic acid which is probably the anhydride of **αβ-di-oxy-phenyl-propionic acid**



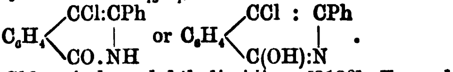
$C_6H_5.\overset{\frown O \frown}{CH\ .\ CH}.CO_2H$ (Erlenmeyer, *B.* 20, 2465), and *αβ*-di-oxy-phenyl-propionic acid.—2. *Sodium amalgam* forms *β*-oxy-phenyl-propionic acid.—3. Fuming HCl produces *αβ*-di-chloro-phenyl-propionic acid.—4. Boiling with Ac_2O gives *α*-chloro-cinnamic acid.

Salt.—AgA′: crystalline powder.

α-Chloro-β-oxy-phenyl-propionic acid $C_6H_5.CH(OH).CHCl.CO_2H$. From *αβ*-di-oxy-phenyl-propionic acid and HCl (Leschhorn, *Dissert. Wurzburg*, 1884). Formed also by the action of HCl on  $C_6H_5.\overset{\frown O \frown}{CH.CH}.CO_2H$, which is obtained by treating the preceding acid with alkalis (Erlenmeyer, jun., *B.* 20, 2466).

Chloro-oxy-α-phenyl-propionic acid $C_9H_9ClO_3$. *Chloro-tropic acid.* [130°]. From atropic acid and aqueous ClOH (Ladenburg, *A.* 217, 110). Crystals; v. e. sol. water. Zinc-dust and iron filings in HOAc convert it into tropic acid.

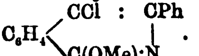
(*Py.* 1:4:2) - **CHLORO - OXY - PHENYL - ISO - QUINOLINE** $C_{15}H_{10}ClNO$ *i.e.*



$C_6H_4<\substack{CCl:CPh\\CO.NH}$ or $C_6H_4<\substack{CCl:CPh\\C(OH):N}$.

Chloro-isobenzalphthalimidine. [212°]. Formed by heating chloro-methoxy-phenyl-isoquinoline [76°] with fuming HCl at 100°. Silky needles. V. sol. benzene, chloroform, and acetic acid, m. sol. cold alcohol and ether (Gabriel, *B.* 19, 2358).

Methyl derivative $C_{16}H_{12}NOCl$ *i.e.*



$C_6H_4<\substack{CCl:CPh\\C(OMe):N}$. [76°]. Formed by heating di-chloro-phenyl-isoquinoline with a solution of sodium in methyl alcohol at 100°. Colourless needles. V. sol. ether, chloroform, benzene, and acetic acid. Very weak base. By heating with fuming HCl at 100° it yields chloro-oxy-phenyl-isoquinoline (chloro-isobenzalphthalimidine) and methyl chloride (Gabriel, *B.* 19, 2357).

TETRA - CHLORO - DI - OXY - DI - PHENYL SULPHONE $C_{12}H_6Cl_4SO_4$ *i.e.* $SO_2(C_6H_2Cl_2.OH)_2$. [289°]. S.G. ^{15} 1·777. From $SO_2(C_6H_4.OH)_2$, $KClO_3$, and HCl (Annaheim, *A.* 172, 38; *B.* 9, 1150). Needles or prisms. Insol. water, v. sl. sol. cold alcohol.

DI - CHLORO - DI - OXY - DI - PHENYL - THIOUREA. ***Di-methyl ether*** $SC(NH.C_6H_3Cl(OMe))_2$. [153°]. From chloro-anisidine, alcohol, and CS_2. White needles, sol. alcohol and ether (Herold, *B.* 15, 1687).

CHLORO-OXY-PICOLINIC ACID *v.* CHLORO-OXY-PYRIDINE CARBOXYLIC ACID.

CHLORO-OXY-PROPANE SULPHONIC ACID $C_3H_7ClSO_4$ *i.e.* $CH_2Cl.CH(OH).CH_2.SO_3H$. From epichlorhydrin and Na_2SO_3 at 100° (Darmstädter, *A.* 148, 126). Syrup.—NaA′2aq: monoclinic crystals.—NaA′ aq: trimetric tables. -NaA′ ½aq (Pazschke, *J. pr.* [2] 1, 94).—CaA′$_2$ 6aq.— BaA′$_2$ aq. PbA′$_2$ 2aq.—AgA′ 3aq.

β-CHLORO-α-OXY-PROPIONIC ACID $CH_2Cl.CH(OH)CO_2H$. *Chloro-lactic acid.* [78°].

Formation.—1. From chloro-acetic aldehyde by treatment with HCN and HCl (Glinsky, *Z.* 1870, 515; Frank, *A.* 206, 344).—2. Together with its isomeride by the union of HOCl with acrylic acid in aqueous solution at 0° (Melikoff, *B.* 13, 2153).

Preparation.—Epichlorhydrin (5 g.) is heated with (20 g. of) nitric acid (S.G. 1·38) on a water bath until the odour of chloropicrin is perceived. The product is poured into water and extracted with ether. On evaporation this leaves an oil that solidifies over H_2SO_4 (v. Richter, *J. pr.* 128, 193).

Properties.—Flat, deliquescent prisms. V. sol. water, alcohol, and ether. Cannot be distilled. Moist Ag_2O converts it into glyceric acid. When heated with water it splits up into aldehyde, CO_2, and HCl (Erlenmeyer, *B.* 13, 309).

Salts.—CaA′$_2$ 3aq.—ZnA′$_2$ 3aq.—MnA′$_2$ 3aq. CuA′$_2$.—AgA′.

Methyl ether MeA′: (186°); liquid.

Ethyl ether EtA′. [37°]. (205°).

α-Chloro-β-oxy-propionic acid $CH_2OH.CHCl.CO_2H$.

Formation.—1. From glyceric acid and HCl (Werigo a. Melikoff, *B.* 12, 178).—2. From acrylic acid and HOCl.—3. By the action of water on αβ-di-chloro-propionic acid (Melikoff, *B.* 12, 2227).—4. From oxy-acrylic acid and HCl (Melikoff, *B.* 13, 273).

Properties.—Syrup. V. sol. water, alcohol, and ether. Converted by moist Ag_2O into glyceric acid, and by alcoholic KOH into oxy-acrylic acid. Conc. HCl forms, at 100°, αβ-di-chloro-propionic acid [50°]. Zinc and dilute H_2SO_4 reduce it to hydracrylic acid (Melikoff, *J. R.* 13, 164).

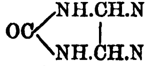
Salt.—ZnA′$_2$: hygroscopic gummy mass.

Di-chloro-oxy-propionic acid $CHCl_2.CH(OH).CO_2H$. [77°]. From di-chloro-acetic aldehyde, HCN, and HCl (Grimaux a. Adam, *B.* 10, 903; *Bl.* [2] 34, 29). Deliquescent tables; v. e. sol. water, alcohol, and ether. Reduces ammoniacal $AgNO_3$.

Ethyl ether EtA′. (220°). From the acid. Also from tri-chloro-oxy-propionic ether in alcoholic solution, by treatment with zinc, and HCl (Pinner a. Bischoff, *A.* 179, 88).

Tri-chloro-oxy-propionic acid $CCl_3.CH(OH).CO_2H$. *Tri-chloro-lactic acid.* [105°-110°]. From its nitrile by HCl (Pinner, *A.* 179, 79; *B.* 17, 1997). Prisms; sol. ether. Split up by alkalis into chloral and formic acid.

Reactions.—1. With strong aqueous NH_3 it gives glycosine.—2. With *hydroxylamine* it yields glyoxim.—3. With *phenyl-hydrazine* it yields glyoxal-di-phenyl-hydrazide.—4. With *urea* and a little water it gives acetylene-urea $C_4H_6N_4O_2$ *i.e.*



$$OC\begin{matrix}\diagup NH.CH.NH \diagdown\\ \qquad | \qquad\\ \diagdown NH.CH.NH \diagup\end{matrix}CO$$

(Pinner, *B.* 17, 1997).—5. Fusion with *urea* forms some uric acid (Horbaczewski, *M.* 8, 584).

Salts.—NH_4A'.—KA′: prisms.

Ethyl ether EtA′. [67°]. (c. 235°). Formed by heating chloralide with alcohol (Wallach, *A.* 193, 8).

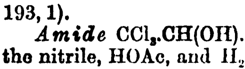
Preparation.—Chloral-hydrate is converted into its cyanhydrin by mixing with strong HCN, and after 24 hrs. standing the mixture is digested on the water-bath for 4-6 hrs. and evaporated. The crystalline cyanhydrin is dissolved in one-third its weight of alcohol and HCl gas led into the boiling solution. When the reaction is complete the ether is precipitated by water, and solidifies on cooling; the yield is 90 p.c. of the theoretical (Pinner, *B.* 18, 754).

Properties.—Insol. water. Converted by alkalis into tartronic acid. Zinc and HCl reduce it, in alcoholic solution, to di-chloro-oxy-propionic acid.

Acetyl derivative $CCl_3.CH(OAc).CO_2H$. [65°].

Tri-chloro-ethylidene ether *v.* CHLORALIDE.

Tri-bromo-ethylidene ether



$$CBr_3.CH\begin{matrix}\diagup O.CO \diagdown\\ \diagdown O \qquad\diagup\end{matrix}CH.CCl_3$$

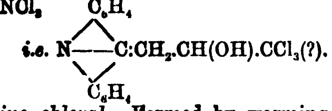
[149°] (Wallach, *A.* 193, 1).

Amide $CCl_3.CH(OH).CONH_2$. [96°]. From the nitrile, HOAc, and H_2SO_4 (Pinner a. Fuchs, *B.* 10, 1061). Slender needles; v. sol. cold water. **Acetyl derivative** $CCl_3.CH(OAc).CO.NH_2$. [95°].

Nitrile $CCl_3.CH(OH).CN$. [61°]. (c. 218°). From chloral and HCN (Hagemann, *B.* 5, 151; Pinner a. Bischoff, *A.* 179, 77; 17, 1997). Trimetric tables (from CS_2). V. sol. water, alcohol, and ether. *Reactions.*—1. Alkalis split it up into chloroform, HCy, and formic acid.—2. Ammonia forms di-chloro-acetamide.—3. Heated with *urea* it yields tri-chloro-ethylidene-di-ureide $CCl_3.CH(NH.CO.NH_2)_2$ as chief product, and biuret as a by-product (Pinner a. Lifschutz, *B.* 20, 2345).

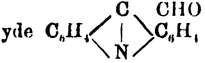
Acetyl derivative $CCl_3.C(OAc).CN$. [31°]. (208°).

ω-TRI-CHLORO-β-OXY-(*A.*)-PROPYL-ACRIDINE $C_{16}H_{12}ONCl_3$ *i.e.*



$$N\begin{matrix}\diagup C_6H_4 \diagdown\\ \text{———}\\ \diagdown C_6H_4 \diagup\end{matrix}C:CH_2.CH(OH).CCl_3(?)$$

Methyl-acridine chloral. Formed by warming (*A.*)-methyl-acridine (60 g.) suspended in benzene (600 g.) with anhydrous chloral (70 g.); at 70°-75° the product separates as a sandy pp.; the yield is nearly theoretical. Yellow needles or prisms. Above 200° it is again resolved into methyl-acridine and chloral. Sl. sol. all ordinary solvents. Its basic properties are very slight. The solution in conc. H_2SO_4 has a splendid greenish-yellow fluorescence. By alkalis it is partially resolved into methyl-acridine and chloral, and partly converted into acridyl-acrylic acid $C_{13}H_8N.CH{:}CH.CO_2H$ whence $KMnO_4$ produces acridine-(*A.*)-aldehyde



$$\mathrm{C_6H_4}\!\left\langle\begin{array}{c}\mathrm{C\;\;CHO}\\ |\\ \mathrm{N}\end{array}\right\rangle\!\mathrm{C_6H_4}$$

[140°] (Bernthsen a. Muhlert, *B.* 20, 1542).

DI-CHLORO-OXY-PYRIDINE $C_5H_2(OH)Cl_2N$ [178°]. Formed by heating the ethyl ether with HCl (Koenigs a. Geigy, *B.* 17, 1834). Colourless crystals. V. sol. hot water.

Ethyl ether $C_5H_2(OEt)Cl_2N$: [31°]; white crystals; formed by heating tri-chloro-pyridine with sodium ethylate.

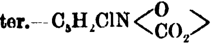
CHLORO-(γ)-OXY-PYRIDINE CARBOXYLIC ACID $C_5H_2ClN(OH)(CO_2H)$. *Chloro-oxy-picolinic acid.* S 4 at 100°.

Preparation.—Comenamic acid (*q.v.*) is heated with PCl_5 (5 equivalents) in a sealed tube at 220°. The product is poured into water at 0°. The oil that separates is extracted with hot water and the extract evaporated to crystallisation. The crystals are dissolved in a little hot water and NH_3 is added: ammonic comenate separates and calcic chloride is then added to the filtrate. Calcic chloro-oxy-methyl pyridine carboxylate crystallises out slowly (Bellmann, *J. pr.* [2] 29, 3).

Properties.—Pointed needles (containing aq). Insol. cold water, ether, chloroform, and benzene. Sol alcohol and acids.

Reactions.—1. Fe_2Cl_6 gives a brown pp. sol. excess.—2. $AgNO_3$ gives a bulky white pp. soon becoming granular.—3. Reduced by Sn and HCl to (γ)-oxy-pyridine carboxylic acid ((γ)-oxy-picolinic acid).

Salts. B'HCl. Very soluble pointed needles. CaA'_2 aq. Got by adding $CaCl_2$ to a solution of the acid nearly neutralised by NH_3. M. sol. water.—



$$\mathrm{C_5H_2ClN}\!\left\langle\begin{array}{c}\mathrm{O}\\ \mathrm{CO_2}\end{array}\right\rangle\!\mathrm{Ca}$$

$\frac{1}{2}$aq. Got by adding $CaCl_2$ to a solution of the acid quite neutralised by NH_3.

Chloro-oxy-pyridine carboxylic acid $C_5H_2ClN(OH)CO_2H$. *Chloro-oxy-picolinic acid.* [c. 257°]. Obtained by heating penta chloro-methyl-pyridine $C_5H_2Cl_2N.CCl_3$ with H_2SO_4 (Ost, *J. pr.* [2] 27, 257). Thick needles (containing aq). Reduced by HI in acetic acid to (β)-oxy-picolinic acid.

Salt. CaA'_2 4aq.

Chloro-oxy-pyridine carboxylic acid $C_5H_2ClN(OH).CO_2H$. *Chloro-oxy-picolinic acid.* Obtained by the action of H_2SO_4 on penta-chloro-methyl-pyridine obtained by treating picolinic acid with PCl_5 (Seyffertli, *J. pr.* [2] 34, 254). Clusters of needles. Does not melt below 315°. Sl. sol. cold water. Does not combine with HCl.

Chloro-oxy-pyridine carboxylic acid $C_5H_2ClN(OH)CO_2H$. *Chloro-oxy-nicotinic acid.* [302°]. From nicotinic acid by successive treatment with PCl_5 and H_2SO_4. Monoclinic prisms (S.).

Di-chloro-oxy-pyridine carboxylic acid $C_5HCl_2N(OH)CO_2H$. *Di-chloro-oxy-picolinic acid.* [c. 282°].

Preparation.—By heating hexa-chloro-methyl-pyridine $C_5HCl_2N.CCl_3$ with (80 p.c.) H_2SO_4 (Ost, *J. pr.* [2] 27, 257).

Properties.—Felt-work of fine needles (containing aq) (from water), or else as small hard prisms. Decomposes about 282°. Not attacked by Sn and HCl or by aqueous HI. Reduced by HI in glacial acetic acid to (α)-oxy-picolinic acid.

Salts.—Mostly soluble, except the calcium salt, CaA'_2, which is but slightly soluble, although it is more soluble than the acid. Separates by spontaneous evaporation as silvery stars.

CHLORO-OXY-PYROTARTARIC ACID $C_5H_7ClO_5$. *Chloro-citramalic acid.* [100°].

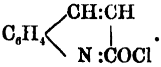
Formation.—1. From citraconates and HClO (Carius, *A.* 126, 204).—2. From citra- or mesa-di-chloro-pyrotartaric acid by warming with water (Gottlieb, *A.* 160, 101; Morawski, *J. pr.* [2] 10, 68; 11, 466).—3. By passing chlorine into an aqueous solution of sodium mesaconate (Morawski, *J. pr.* [2] 12, 392).

Properties.—Trimetric crystals. Water at 120° converts it into di-oxy-pyrotartaric acid and acetone.

Salts.—BaA'' aq: monoclinic tables, v. sl. sol. cold water.—PbA'' 4aq.—Ag_2A''.

Chloro-oxy-pyrotartaric acid $C_5H_7ClO_5$. *Hydro-chloro-oxy-citraconic acid.* [162°]. From oxy-citraconic acid and fuming HCl at 120° (Morawski, *J. pr.* [2] 11, 443). Plates. Split up by bases into HCl and oxy-citraconic acid. Sodium amalgam reduces it to oxy-pyrotartaric acid *q.v.*

CHLORO-OXY-QUINOLINE C_9H_6NOCl ***i.e.***

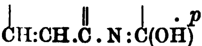


$$\mathrm{C_6H_4}\!\left\langle\begin{array}{l}\mathrm{CH{:}CH}\\ \qquad |\\ \mathrm{N{:}COCl}\end{array}\right.$$

. [112°]. Formed by the action of bleaching powder solution on the borate of quinoline (Einhorn a. Lauch, *A.* 243, 313). White prismatic needles. Sol. hot water, acetic ether, HOAc.

Reactions.—1. Boiled in an alkaline solution carbostyril is formed.—2. PCl_5 forms (*Py.* 3) chloro-quinoline.—3. Boiled with alcohol *p*-chloro-carbostyril [263°] is formed.

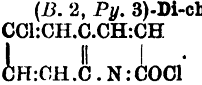
(*B.* 2)-**Chloro-**(***Py.*** 3)-**oxy-quinoline**



$$\begin{array}{l}\mathrm{CCl{:}CH.C.CH{:}CH}\\ |\qquad\quad\;\|\qquad\;|\\ \mathrm{CH{:}CH.C\,.\,N{:}C(OH)}\end{array}$$

. *p-Chloro-carbostyril.* [263°]. Formed by treating the following body with alkalis, and, by intramolecular change, from the preceding body. When its alkaline solution mixed with NaOCl is treated with CO_2 the following body is ppd. $KMnO_4$ gives *p-chloro-isatin* [248°].

(*B.* 2, *Py.* 3)-**Di-chloro-**(***Py.*** 3)-**oxy-quinoline**



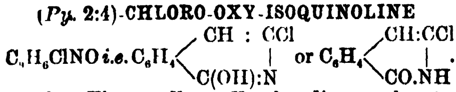
$$\begin{array}{l}\mathrm{CCl{:}CH.C.CH{:}CH}\\ |\qquad\quad\;\|\qquad\;|\\ \mathrm{CH{:}CH.C\,.\,N{:}COCl}\end{array}$$

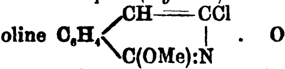
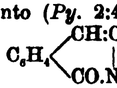
. [115°] and [145°] From (*B.* 2)-chloro-quinoline and bleaching powder (Einhorn a. Lauch, *A.* 243, 353). Plates (from HOAc) or needles (from EtOAc). Dimorphous. Boiling alkalis give chloro-carbostyril [263°].

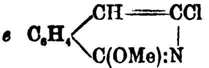
Chloro-oxy-quinoline *v.* CHLORO-CARBOSTYRIL.

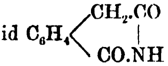
Tri-chloro-oxy-quinoline $C_9H_4Cl_3ON$. [200°]. Prepared by passing chlorine for 6 hours into a solution of quinoline in dilute acetic acid. The product is crystallised from alcohol. The yield is 15 p.c., most of the quinoline being recovered. Thin matted needles, sol. benzene, chloroform, and alcohol. Reduced by HI at 250° to oxy-quinoline, which is found to be (*Py.* 3)-oxy-quinoline (J. Rotheit, *J. pr.* [2] 29, 300).

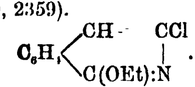
(*Py.* 2:4)-CHLORO-OXY-ISOQUINOLINE


C_9H_6ClNO *i.e.* $C_6H_4<\begin{array}{l}CH:CCl\\ \quad|\\ C(OH):N\end{array}$ or $C_6H_4<\begin{array}{l}CH:CCl\\ \quad|\\ CO.NH\end{array}$.

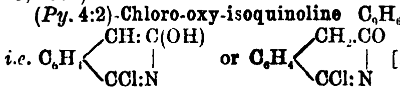
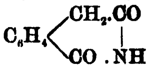
[220°]. Fine needles. V. sol. ordinary solvents. Dissolves in dilute NaOH. Formed as a by-product in the action of alcoholic KOH upon di-chloro-isoquinoline. Obtained by the action of dry HCl gas at c. 150° upon (*Py.* 2:4)-chloro-methoxy-isoquinoline  $C_6H_4<\begin{array}{l}CH=CCl\\ \quad|\\ C(OMe):N\end{array}$. On methylation with MeI and methyl alcoholic KOH, it is converted into (*Py.* 2:4:3)-chloro-oxy-methyl-isoquinoline  $C_6H_4<\begin{array}{l}CH:CCl\\ \quad|\\ CO.NMe\end{array}$, isomeric with the above chloro-methoxy-isoquinoline (Gabriel, *B.* 19, 2360).

Methyl derivative  $C_6H_4<\begin{array}{l}CH=CCl\\ \quad|\\ C(OMe):N\end{array}$.

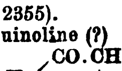
[74°]. Formed by heating di-chloro-isoquinoline with a solution of sodium in methyl alcohol, at 100°. Thick needles. V. sol. alcohol, ether, &c. By digestion with fuming HCl at 100° it is converted into the imide of phenyl-acetic-*o*-carboxylic acid  $C_6H_4<\begin{array}{l}CH_2.CO\\ \quad|\\ CO.NH\end{array}$ (di-oxy-isoquinoline). By dry HCl at 150° it is converted into chloro-oxy-isoquinoline (Gabriel, *B.* 19, 2359).

Ethyl derivative  $C_6H_4<\begin{array}{l}CH-CCl\\ \quad|\\ C(OEt):N\end{array}$.

[37°]. Formed by heating di-chloro-isoquinoline with alcoholic sodium ethylate at 100°. Long needles. V. sol. ordinary solvents (Gabriel, *B.* 19, 2358).

(*Py.* 4:2)-Chloro-oxy-isoquinoline C_9H_6ClNO *i.e.*  $C_6H_4<\begin{array}{l}CH:C(OH)\\ \quad|\\ CCl:N\end{array}$ or $C_6H_4<\begin{array}{l}CH_2.CO\\ \quad|\\ CCl:N\end{array}$ [197°]. Formed as a by-product in the preparation of di-chloro-isoquinoline by the action of $POCl_3$ at 150°-170° upon the imide of phenyl-acetic-*o*-carboxylic acid  $C_6H_4<\begin{array}{l}CH_2.CO\\ \quad|\\ CO.NH\end{array}$ (di-oxy-isoquinoline). Long thick needles, or colourless plates. M. sol. hot alcohol, sl. sol. ether, cold acetic acid, hot benzene, and chloroform.

Methyl derivative $C_9H_5(CH_3)NO$: [67°]. Small white crystals; v. sol. alcohol, ether, &c., insol. alkalis. Formed by heating chloro-oxy-isoquinoline with MeI and methyl-alcoholic KOH (Gabriel, *B.* 19, 2355).

Di-chloro-oxy-isoquinoline (?) $C_9H_5Cl_2NO$ probably  $C_6H_4<\begin{array}{l}CO.CHCl\\ \quad|\\ CCl:N\end{array}$. Formed by heating hippuric acid with PCl_5. By further action of PCl_5 it is converted into a body $C_9H_5NCl_6$, [184°] (Rügheimer, *B.* 19, 1169; *cf.* Schwanert, *A.* 112, 59).

DI-*p*-CHLORO-DI-OXY QUINONE $C_6Cl_2(OH)_2O_2$ [1:4:2:5:3:6]. ***Chloranilic acid*** (Hantzsch, *B.* 20, 1303, 2279).

Formation.—1. By dissolving tetra-chloro-quinone (chloranil) in dilute aqueous KOH (Erdmann, *J. pr.* 22, 281; *cf.* Stenhouse, *A. Suppl.* 8, 14).—2. By the action of potash on tri-chloro-quinone (Graebe, *A.* 146, 24).

Properties.—Glittering red plates (containing aq). May be partially sublimed. Its aqueous solution is violet, but decolourised by HCl or H_2SO_4, by which it is ppd.

Reactions.—1. *Reduced* by tin and HCl to di-chloro-tetra-oxy-benzene.—2. PCl_5 forms tetra-chloro-quinone.—3. By treatment with *bromine* it is converted into di-chloro-tetra-bromo-acetone $CBr_2Cl.CO.CBr_2Cl$ [79°] (Levy a. Jedlička, *B.* 20, 2318; *cf.* Stenhouse, *A. Suppl.* 8, 17).—4. HCl and $KClO_3$ form tetra-chloro-acetone $CHCl_2.CO.CHCl_2$, which crystallises with 4aq [49°] (Levy a. Jedlička, *B.* 21, 318).—5. *Ammonia* forms $C_6Cl_2O_2(NH_2)(OH)$ 3aq crystallising in black needles and forming the salts $C_6Cl_2O_2(NH_2)(ONH_4)$ 4aq and $C_6Cl_2O_2(NH_2)(OAg)$. 6. A small quantity of SO_2 forms tetra-chloro-tetra-oxy-quinhydrone $C_{12}H_6Cl_4O_8$, crystallising in black needles.

Salts.—$K_2C_6Cl_2O_4$ aq: purple prisms, forming a purple solution in water or alcohol.—Na_2A''4aq: dark crimson needles (Hesse, *A.* 114, 304).—BaA''3aq: red-brown scales.—Ag_2A'': red pp.

Di-ethyl ether $Et_2C_6Cl_2O_4$. Red prisms (from alcohol).

CHLORO-DI-OXY-QUINONE SULPHONIC ACID $C_6H_3ClSO_7$ *i.e.* $C_6Cl(OH)_2O_2(SO_3H)$. **Potassium salt** $C_6Cl(OK)_2O_2(SO_3K)$ 2aq. From tri-chloro-hydroquinone sulphonic acid and KOH (Græbe, *A.* 146, 55). Red needles; v. sol. water, insol. alcohol. With HCl it gives yellow laminæ of $C_6Cl(OH)_2O_2(SO_3K)$, decolourised by tin and HCl.

DI-*p*-CHLORO-DI-*p*-OXY-TEREPHTHALIC ACID $C_6Cl_2(OH)_2(CO_2H)_2$ [1:4:2:5:3:6]. From the colourless ether (*v. infra*) and conc. aqueous NaOH at 100°. Greenish-yellow needles (containing 2aq). Stable in the air, but effloresces over H_2SO_4 into the white anhydrous pseudo-form (di-chloro-quinone di-hydro-di-carboxylic acid) which is reconverted into the unstable form by heating with aqueous NaOH.

Ethyl ether. Di-chloro-hydroquinone-di-carboxylic ether. [123°]. Formed by reduction of di-chloro-quinone-di-carboxylic ether $C_6Cl_2O_2(CO_2Et)_2$ with zinc-dust and acetic acid. Long thin colourless needles. V. sol. ether. By melting and quick cooling it is converted into yellowish-green dichroic tables, which are probably the *pseudo-form* $C_6H_2Cl_2O_2(CO_2Et)_2$ (di-chloro-quinone-di-hydro-di-carboxylic ether); this is unstable, and by a gentle warming is converted back into the colourless needles of the stable form (Hantzsch a. Zeckendorf, *B.* 20, 1812).

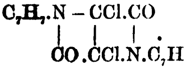
CHLORO-OXY-THYMOQUINONE $C_{10}H_{10}(OH)ClO_2$ *i.e.* $C_6Cl(CH_3)(C_3H_7)O_2(OH)$. [122°]. From di-nitro-thymol by treatment with PCl_5, the chloro-di-nitro-thymol so formed being reduced by tin and HCl and the resulting amido- compound oxidised by CrO_3 (Ladenburg a. Engelbrecht, *B.* 10, 1218). Lemon-yellow prisms (from alcohol). Readily sublimes. Its alkaline solutions are violet. Boiling with KOH converts it into di-oxy-thymoquinone.

CHLORO-OXY-TOLUCARBOSTYRIL *v.* CHLORO-DI-OXY-METHYL-QUINOLINE.

CHLORO-OXY-TOLUQUINOLINE *v.* CHLORO-OXY-METHYL-QUINOLINE.

DI-CHLORO-DI-OXY-TOLUQUINONE (?) $C_7H_4Cl_2O_3$ *i.e.* $C_6Cl_2Me(OH)O_2$. [157°]. From **tri-chloro-orcin** and alkaline K_4FeCy_6 (Stenhouse a. Groves, *B.* 13, 1306). Deep yellow scales (from water). Sl. sol. water, v sol. alcohol. Reduced by SO_2 to colourless $C_7H_6Cl_2O_3$, which on oxidation gives purplish-brown crystals of a quinhydrone. A di-chloro-di-oxy-toluquinone has been described by Bräuninger (*A.* 185, 339) as obtained from beech-wood creosote by treatment with $KClO_3$ and HCl; the resulting tetra-chloro-toluquinone being reduced by SO_2 to the **tetra-chloro-hydrotoluquinone**, whence dilute KOH forms di-chloro-di-oxy-toluquinone, a brick-red crystalline powder.

DI-CHLORO-DI-OXY-DI-*o*-TOLYL-PYRAZINE



$$\begin{array}{l} C_7H_7.N-CCl.CO \\ \quad\ \ | \quad\ \ | \quad\ \ | \\ \quad CO.CCl.N.C_7H_7 \end{array}$$

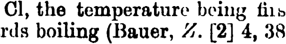
[201°]. From di-oxy-di-tolyl-pyrazine dihydride and PCl_5 (Abenius a. Widmann, *B.* 21, 1662).

CHLORO-OXY-VALERIC ACID $C_3H_5Cl(OH).CH_2.CO_2H$. Obtained by oxidising chloro-allyl-propyl alcohol by chromic mixture (Lopatkin, *J. pr.* [2] 30, 396). Crystalline.

Salts.—$BaA'_2$8aq. —NaA'aq.

γ-Chloro-γ-oxy-valeric acid

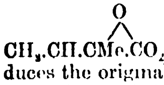
Lactone. $C_5H_7O_2Cl$ *i.e.*



$CH_3.\underline{CCl.CH_2.CH_2.CO.O}$

(80°-82°) at 10 mm. Got by passing HCl into (*a*)-angelico-lactone. Decomposed by water into HCl and levulic acid. On distillation it splits up into HCl and (*β*)-angelico-lactone Bromine converts the lactone into brominated bodies, whence water forms a great deal of di-bromo-levulic acid and some bromo-levulic acid (Wolff, *A.* 229, 249).

Chloro-oxy-valeric acid $C_5H_9ClO_3$ *i.e.* $CH_3.CHCl.CMe(OH).CO_2H$. [75°]. Formed, together with its isomeride, by the union of tiglic acid with HOCl (Melikoff, *A.* 234, 225; *Bl.* [2] 47, 166). Needles, sol. water, alcohol, and ether. Alcoholic KOH converts it into butylene oxide carboxylic (di-methyl-glycidic) acid



$CH_3.\overset{\frown O \frown}{CH.CMe}.CO_2H$

[62°], whence HCl reproduces the original acid [75°].

Salts.- ZnA'_2.- CaA'_2: prisms.

Chloro-oxy-valeric acid $CH_3.CH(OH).CMeCl.CO_2H$. [112°]. Formed, together with the preceding, by the union of HOCl with tiglic acid (M.). Prisms; v. sol. water, alcohol, and ether. Alcoholic KOH converts it into the same butylene oxide carboxylic acid as the preceding.

Salts.- These are gummy masses.—ZnA'_2.—CaA'_2.- BaA'_2.

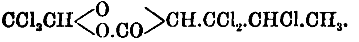
Tri-chloro-oxy-valeric acid $CH_3.CHCl.CCl_2.CH(OH).CO_2H$. [140°]. Prepared by boiling with HCl the compound of tri-chloro-butyric aldehyde with HCN (Pinner a. Klein, *B.* 11, 1492; *A.* 179, 99). Trimetric tables, v. sol. alcohol, ether, and hot water.

Salts.—NaA'aq: crystals.- PbA'_2: amorphous pp.

Ethyl ether EtA'. [40°]. (255°). Long prisms. Alcoholic NH_3 converts it into $C_5H_7ClN_2O$ (? amide of chloro-imido-angelic acid) [118°] whence boiling alcohol produces $C_5H_6ClNO_2$.

Acetyl derivative $C_5H_6AcCl_3O_3$ aq. [84°]. Slender needles.

Tri-chloro-ethylidene ether



$CCl_3CH{<}\begin{smallmatrix}O\\O.CO\end{smallmatrix}{>}CH.CCl_2.CHCl.CH_3$.

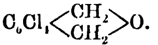
[87°]. (297°). From the acid and chloral at 175° (Wallach, *A.* 193, 37) Thick crystals (from chloroform); explodes when struck.

Amide $CH_3.CHCl.CCl_2.CH(OH).CO.NH_2$ [119°]. Sl. sol. water and C_6H_6, v. sol alcohol and ether. Prepared by the action of strong H_2SO_4 on the nitrile (Pinner a Klein, *B.* 11, 1490).

Nitrile $CH_3.CHCl.CCl_2.CH(OH).CN$. *Butyl-chloral cyanhydrin.* [102°]. (c. 230°). From tri-chloro-butyric orthaldehyde, alcohol, and conc. HCyAq. Leaflets (from dilute HClAq); m. sol. cold water, v. sol. alcohol. Converted by alcoholic NH_3 into the amide of (*β*)-chloro-crotonic acid. Urea gives chloro-crotonyl-urea $C_3H_4Cl.CONH.CO.NH_2$ and butyro-chloral biuret.

Acetyl derivative of the nitrile $CH_3.CHCl.CCl_2.CH(OAc).CN$. (240°-252°). From the nitrile and AcCl. Yellowish oil.

TETRA-CHLORO-*ω*-DI-OXY-XYLENE. *Anhydride* $C_8H_4Cl_4O$ *i.e.*



$C_6Cl_4{<}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}{>}O$.

[218°]. From tetra-chloro-phthalic acid (7·7 g.), conc. HI (3·5 c.c.) and red phosphorus (2 g.) at 230° (Graebe, *A.* 238, 331). Needles (from toluene). Sl. sol. hot alcohol, m. sol. hot benzene or HOAc. Insol. boiling alkalis.

CHLORO-PENTANE *v.* AMYL CHLORIDE.

Di-chloro-pentane $C_5H_{10}Cl_2$. *Amylene chloride.* (145°). S.G. $\frac{0}{0}$ 1·22; $\frac{0}{0}$ 1·058. From crude amylene and PCl_5 (Guthrie, *C. J.* 14, 128; *A.* 121, 115) or Cl, the temperature being first at −15°, afterwards boiling (Bauer, *Z.* [2] 4, 380, 667; *cf.* Kondakoff, *C. C.* 1887, 979).

Di-chloro-pentane $(CH_3)_2CH.CH_2.CHCl_2$. *Isoamylidene chloride.* (130°). S.G. ^{24} 1·05. From isovaleric aldehyde and PCl_5 (Ebersbach, *A.* 106, 265). KOH gives $(CH_3)_2CH.CH:CHCl$ (86°) and $(CH_3)_2CH.C⋮CH$ (Bruylants, *B.* 8, 413).

aa-Di-chloro-pentane $CH_3.CH_2.CH_2.CCl_2.CH_3$. From methyl propyl ketone and PCl_5 (Bruylants, *B.* 8, 411). Liquid; decomposed by distillation. Dry KOH forms $CH_3.CH_2.CH_2.C⋮CH$. Alcoholic KOH forms $CH_3.CH_2.CH_2.CCl:CH_2$ (96°) and $CH_3.C⋮C.C_2H_5$ (Favorsky, *Bl.* [2] 45, 247).

Di-chloro-pentane $C_5H_{10}Cl_2$. (155°-160°). S.G. ^{0} 1·19. Formed by chlorination of ordinary amyl chloride (Buff, *A.* 148, 350).

Di-chloro-pentane $C_5H_{10}Cl_2$. (151°). From valerylene and HCl at 100° (Reboul, *Z.* 1867, 173). Heavy oil.

Tri-chloro-pentane $C_5H_9Cl_3$. (185°-190°). S.G. ^{13} 1·33. By chlorination of ordinary amyl chloride (Buff, *A.* 148, 350). A crystalline tri-chloro-pentane is formed (160°-190°) by chlorinating crude amylene (Bauer, *J. pr.* 100, 42).

Tetra-chloro-pentane $C_5H_8Cl_4$. (240°). S.G. ^{0} 1·429. From amylene and Cl (Bauer, *J. pr.* 100, 43).

Penta- and Hexa-chloro-pentanes have been obtained by Spring a. Lecrenier (*Bl.* [2] 48, 623) by chlorinating isoamyl mercaptan.

CHLORO-ISO-PENTANE SULPHONIC ACID $C_5H_{10}Cl.SO_3H$. From isopentane sulphonic acid and Cl in sunshine or, in presence of iodine, at 130° (Spring a. Winssinger, *B.* 17, 537; *Bl.* [2] 41, 301).—BaA'_2.

CHLORO-PENTENOIC ACID *v.* Chloro-angelic acid and Chloro-tiglic acid.

CHLORO-PENTENYL ALCOHOL $CH_2.CH:CCl.CHMe.OH$. *Methyl-chloro-allyl carbinol.* (159°) at 725 mm. S.G. $\frac{14·1}{14·1}$ 1·0882. V.D. 4·09 (Theory 4·17). From tri-chloro-amyl-alcohol $C_3H_4Cl_3.CHMe.OH$, finely divided iron, and acetic acid (Garzarolli-Thurnlackh, *A.* 223, 154), or zinc-dust and dilute HCl. Colourless mobile liquid with pungent smell, faintly soluble in water, soluble in ether, CS_2, and chloroform. Combines with bromine. Acetic acid is among the products of oxidation by chromic mixture.

Acetyl derivative C_5H_8AcClO. (173°) at 735 mm. V.D. 5·73 (for 5·66). Does not combine with bromine.

PER-CHLORO-PENTINENE C_5Cl_8. *Per-chloro-mecylene.* [39°]. From comenic acid and PCl_5 at 280° (Ost, *J. pr.* [2] 27, 293). Prisms (from alcohol); smells like camphor. Begins to distil with decomposition at 270°.

CHLORO-PHENANTHRENE *v.* Phenanthrene.

CHLORO-PHENETOL *v.* *Ethyl ether* of Chloro-phenol.

***o*-CHLORO-PHENOL** $C_6H_4Cl(OH)$ [2:1]. [7°]. (176° i.V.).

Formation.—1. From *o*-amido-phenol by displacing NH_2 by Cl by the diazo- reaction (Schmitt a. Cook, *B.* 1, 67; Faust a. Müller, *B.* 5, 777). Solution of $NaNO_2$ is run into a hot solution of *o*-amido-phenol and Cu_2Cl_2 in dilute HCl (Sandmeyer, *B.* 17, 2651).—2. Together with the *p*-isomeride by passing chlorine into phenol (F. a. M.; Krämers, *A.* 173, 331).—3. From *o*-chloro-aniline by displacing NH_2 by OH through the diazo- reaction (Beilstein a. Kurbatoff, *A.* 176, 39).—4. Formed by neutralising with acid a mixture of sodium hypochlorite and phenol (Chandelon, *B.* 16, 1749).

Properties.—Colourless liquid; sl. sol. water, v. sol. alcohol and ether. Potash-fusion converts it into pyrocatechin (Petersen, *B.* 6, 368). HNO_3 gives two chloro-nitro-phenols [111°] and [70°]. PCl_5 gives *o*-di-chloro-benzene (179°).

Methyl ether $C_6H_4Cl(OMe)$. *o-Chloro-anisol.* (203°). Prepared from *o*-anisidine $C_6H_4(NH_2)(OMe)$ by Sandmeyer's reaction (Wallach a. Hensler, *A.* 243, 237; *cf.* Fischli, *B.* 11, 1463).

Ethyl ether $C_6H_4Cl(OEt)$. *o-Chloro-phenetol.* (208°).

Benzoyl derivative $C_6H_4Cl.OBz$. (314°).

Phthalyl derivative $C_6H_4C_2O_2(OC_6H_4Cl)_2$. [98°] (Mosso, *C. C.* 1887, 1396).

m-Chloro-phenol $C_6H_4Cl(OH)$[3:1]. [28·5°]. (214° i. V.). From *m*-chloro-aniline by displacing NH_2 by OH through the diazo reaction (Beilstein a. Kurbatoff, *A.* 176, 45; Uhlemann, *B.* 11, 1161; Varnholt, *J. pr.* [2] 36, 26). White needles.

Benzoyl derivative $C_6H_4Cl(OBz)$. [86°].

Phthalyl derivative [108°] (Mosso).

p-Chloro-phenol $C_6H_4Cl(OH)$[4:1]. [37°]. (217°).

Formation.—1. From phenol and SO_2Cl_2 (Dubois, *Z.* [2] 2, 705; 3, 205).—2. Together with the *o*-isomeride by passing chlorine into cold phenol (D.; Petersen a. Bähr-Praderi, *A* 157, 123).—3. From *p*-amido-phenol by displacing NH_2 by Cl through the diazo- reaction (Schmitt, *B.* 1, 67).—4. From *p*-chloro-aniline by displacing NH_2 by OH through the diazo-reaction (Beilstein a. Kurbatoff, *A.* 176, 30; *B.* 7, 1395).

Properties.—Crystalline; v. sl. sol. water, v. e. sol. alcohol and ether. Insol. aqueous Na_2CO_3. Potash-fusion converts it into hydroquinone and resorcin (Petersen, *B.* 6, 1399; 7, 61; *cf.* Faust, *B.* 6, 1022). PCl_5 gives *p*-di-chloro-benzene [53°]. HNO_3 forms chloro-nitro-phenol [87°].

Salt.—$C_6H_4Cl(ONa)$ (Varnholt, *J. pr.* [2] 36, 19).

Methyl ether $C_6H_4Cl(OMe)$. (c. 200°); S.G. ^{2} 1·182 (Henry, *Z.* [2] 6, 247).

Ethyl ether $C_6H_4Cl(OEt)$. [21°]. (211°).

Benzoyl derivative $C_6H_4Cl(OBz)$. [93°].

Phthalyl derivative $C_6H_4(CO_2C_6H_4Cl)_2$. [11°] (Mosso).

(4:2:1)-Di-chloro-phenol $C_6H_3Cl_2(OH)$[4:2:1] [42°]. (210°).

Formation.—1. By chlorinating phenol (Laurent, *A. Ch.* [2] 63, 27; [3] 3, 210; F. Fischer, *Z.* [2] 4, 386; *A. Suppl.* 7, 180).—2. By adding HCl to a mixture of phenol (1 mol.) and sodium hypochlorite (2 mols.), the (6:2:1)-isomeride is formed simultaneously (Chandelon, *B.* 16, 1751).

Properties.—White needles. Sol. alcohol and ether, nearly insol. water. Expels CO_2 from boiling aqueous Na_2CO_3, but in the cold it is ppd. from its salts by CO_2. PCl_5 gives tri-chloro-benzene [16°].

Salts.—$NH_4O.C_6H_4Cl$: needles (from hot NH_4Aq).—$KA'\ \frac{1}{2}aq$: decomposed by water at 70°, giving off *p*-chloro-phenol.—HOPbA'. AgA'.

Ethyl ether $C_6H_4Cl(OEt)$. (237°).

Acetyl derivative $C_6H_4Cl(OAc)$. (215°).

Benzoyl derivative $C_6H_3Cl_2OBz$. [97°]

Phthalyl derivative $C_6H_4(CO_2C_6H_3Cl_2)_2$ [108°] (Mosso, *Ann. Chim. Farm.* 87, 184).

(6:2:1)-Di-chloro-phenol $C_6H_3Cl_2(OH)$[6:2:1] [63°]. (218°).

Formation.—1. Together with the (4:2:1) isomeride by adding HCl to a mixture of phenol (1 mol.) and sodium hypochlorite (2 mols.) (Chandelon, *B.* 16, 1752).—2. From di-chloro-*p*-amido-phenol by displacing NH_2 by Cl through the diazo- reaction (Seifart, *A. Suppl.* 7, 203; *Z.* [2] 5, 450).

Properties.—Needles. Sol. alcohol and ether, nearly insol. water.

Tri-chloro-phenol $C_6H_2Cl_3(OH)$[6:4:2:1]. [68°]. (244°). S. ·051 at 11°; ·243 at 96°.

Formation.—1. By chlorination of phenol (Laurent, *A. Ch.* [2] 63, 27; [3] 3, 497), of saligenin (the product being distilled with conc. H_2SO_4, Piria, *A.* 56, 47), of aniline (Hofmann, *A.* 53, 8), of indigo (Erdmann, *J. pr.* 19, 332; 22, 276; 25, 472), of phenol sulphonic acid (Vogel, *Z.* 1865, 529), or of phenyl benzyl oxide $C_6H_5O.CH_2Ph$ (Sintenis, *A.* 161, 338).—2. By the action of NaOCl upon (2, 6, 1)-di-chloro-phenol [65°], and upon (2, 4, 1)-di-chloro-phenol [43°] (Chandelon, *Bl.* [2] 38, 123).

Properties.—Needles or prisms. Acid to litmus.

Reactions.—1. HNO_3 forms di-chloro-quinone [120°]; alcohol and N_2O_3 produce the same

body.—2. PCl_5 or Fe_2Cl_6 from tetra-chloro-benzene.—3. HCl and $KClO_3$ give tetra-chloro-quinone. CrO_3 and HOAc produce the same body (Levy a. Schultz, *A.* 210, 160).—4. K_2SO_3 at 170° gives chloro-phenol disulphonic acid and di-chloro-phenol sulphonic acid (Armstrong a. Harrow, *C. J.* 29, 474). 5. Br gives $C_6H_2Cl_3OBr$ [99°] (Benedikt, *M.* 4, 235).

Salts.—$NH_4C_6H_2Cl_3O$: needles; v. sl. sol. cold water.—KA′ ½aq.—MgA'_2 2aq.—BaA'_2 4aq: radiate groups of laminæ.—PbA'_2.—$(PbA'_2)_4PbO$. AgA′: yellow amorphous pp.

Ethyl ether $C_6H_2Cl_3(OEt)$: [44°]. (240°). (Faust, *A.* 149, 152; Lampert, *J. pr.* [2] 33, 381).

Acetyl derivative $C_6H_2Cl_3(OAc)$. (262°).

Propionyl derivative $C_6H_2Cl_3O(CO.C_2H_5)$ (263° uncor.), colourless heavy liquid.

Butyryl derivative $C_6H_2Cl_3.O(CO.C_3H_7)$: (274° uncor.).

Valeryl derivative $C_6H_2Cl_3.O(CO.C_4H_9)$: (283° uncor.).

Benzoyl derivative $C_6H_2Cl_3.OBz$: [70°]; colourless needles; sol. alcohol and ether, insol. water.

Phthalyl derivative $C_6H_2Cl_3.O\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_4$: [194°]; v. sol. chloroform, sl. sol. alcohol and ether, insol. water (Daccomo, *B.* 18, 1163).

Tri-chloro-phenol $C_6H_2Cl_3(OH)$. [54°]. (253° uncor.). From tri-chloro-*p*-amido-phenol (Lampert, *J. pr.* [2] 33, 378). Also from phenol and NaOCl (Chandelon, *Bl.* [2] 38, 119). Silky needles (from dilute alcohol). Volatile with steam. HNO_3 gives no quinone, but a nitro-derivative [116°]. PCl_5 gives C_6HCl_5.

Ethyl ether $C_6H_2Cl_3(OEt)$; (216° uncor.).

Acetyl derivative $C_6H_2Cl_3(OAc)$; (259° uncor.).

Tetra-chloro-phenol $C_6H_2Cl_3(OCl)$[6:4:2:1] or $C_6H_2Cl_2(Cl_2)O$. '*Tri-chloro-phenol chloride.*' [119°]. Formed by passing Cl into tri-chloro-phenol suspended in fuming aqueous HCl (Benedikt, *M.* 4, 233). Trimetric pyramids; *a:b:c* = 1:·61:·51. May be distilled. Conc. KOHAq turns the crystals blue, and on boiling forms tri-chloro-phenol. Hot conc. H_2SO_4 gives tri-chloro-phenol and tetra-chloro-quinone.

Penta-chloro-phenol $C_6Cl_5(OH)$ [188°].

Formation.—1. By the action of chlorine on an alcoholic solution of tri-chloro-phenol, chloro-isatin, or di-chloro-isatin (Erdmann, *J. pr.* 22, 272; Laurent, *A. Ch.* [3] 3, 497).—2. From phenol and chloride of iodine (Schutzenberger, *Bl.* [2] 4, 102). 3. By passing chlorine into a mixture of phenol or tri-chloro-phenol and $SbCl_5$ at 200° (Merz a. Weith, *B.* 5, 458; Benedikt a. Schmidt, *M.* 4, 606). 4. Obtained by heating hexa-chloro benzene with a glycerin solution of NaOH at 250°-280°. *Properties*—Sublimes in long white needles. HNO_3 forms tetra-chloro-quinone. PCl_5 gives C_6Cl_6.

Salts.—C_6Cl_5ONa. KA′.—AgA′.

Methyl ether $C_6Cl_5(OMe)$: [108°]; long white needles; v. sol. alcohol; sublimable.

Acetyl derivative $C_6Cl_5(OAc)$: [148°]; fine white needles; v. sol. alcohol; sublimable (Weber a. Wolff, *B.* 18, 335).

Dichloride $C_6Cl_5(OH).Cl_2$ [78½°–80°]. Formed in the chlorination of *m*-chloro-acetanilide in acetic acid (Beilstein, *B.* 11, 2182). Large colourless pillars. Difficultly soluble in 50 p.c. acetic acid, easily in C_6H_6, $CHCl_3$, CS_2, alcohol, &c. Alkalis decompose it entirely. On heating with alcohol per-chloro-phenol is formed.

Hexa-chloro-phenol C_6Cl_6O. [46°]. Formed by passing Cl into a solution of penta-chloro-phenol in dilute HCl (Benedikt a. Schmidt, *M.* 4, 607). Golden-yellow crystals; gives off chlorine on heating. Tin and HCl re-convert it into penta-chloro-phenol.

Dichloride C_6Cl_8O. [102°]. Formed by chlorinating penta-chloro-phenol in acetic acid solution (B. a. S.). Prisms (from ligroin).

Hexa-chloro-phenol C_6Cl_6O. [106°]. From penta-chloro-aniline by chlorination in acetic acid solution (Langer, *A.* 215, 122). Yellowish prisms (from ligroin).

Per-chloro-diphenol *v.* OCTO-CHLORO-DI-OXY-DIPHENYL.

***o*-CHLORO-PHENOL (γ)-SULPHONIC ACID** $C_6H_5ClSO_4$ *i.e.* $C_6H_3Cl(OH)SO_3H$. From *o*-chloro-phenol and fuming H_2SO_4 (Krämers, *A.* 173, 331). Small colourless plates or cubes (containing aq). V. e. sol. water and alcohol. It begins to decompose at 80°. Fe_2Cl_6 colours its solutions violet. HNO_3 forms chloro-di-nitro-phenol [111°].

Salts.—KA′ ½aq: S. (of KA′) 14 at 9°.—$K_2C_6H_3ClSO_4$ 3½aq: deliquescent laminæ.—NaA′ aq.—$Na_2C_6H_3ClSO_4$ 3aq.—CaA'_2 aq.—$CaC_6H_3ClSO_4$ 3½aq: efflorescent crystalline aggregates; S. 38 at 12°.—BaA'_2 1½aq: granular aggregates of crystals. PbA'_2 4aq.—$PbC_6H_3ClSO_4$ aq.—CuA'_2 4aq: bluish-green trimetric prisms.

***o*-Chloro-phenol (δ)-sulphonic acid** $C_6H_3Cl(OH)SO_3H$. Formed, together with the preceding, when the sulphonation is effected in the cold by fuming H_2SO_4 (1 pt.) mixed with conc. H_2SO_4 (1½ pts.) (K.).—KA′: small plates. $CaC_6H_3ClSO_4$ 2aq: small needles; S. 2·25 at 11°.

***o*-Chloro-phenol (β)-sulphonic acid** $C_6H_3Cl(OH)SO_3H$. Obtained, in small quantity, in sulphonating impure *p*-chloro-phenol (Petersen a. Baehr-Praderi, *A.* 157, 129). Potash-fusion gives pyrogallol. Fe_2Cl_6 colours its neutral solutions violet. HNO_3 gives chloro-di-nitro-phenol [81°].—KA′: stellate groups of short prisms; less soluble than potassium *p*-chloro-phenol sulphonate.

***p*-Chloro-phenol (α)-sulphonic acid** $C_6H_3Cl(OH)(SO_3H)$. [76°]. From *p*-chloro-phenol and fuming H_2SO_4 at 100° (Petersen a. Baehr-Praderi, *A.* 157, 121). Glittering plates (containing aq). Begins to decompose at 100°. Gives a bluish-violet colour with Fe_2Cl_6. Potash-fusion gives pyrogallol and a trace of hydroquinone. HNO_3 forms chloro-nitro-phenol sulphonic acid (Armstrong, *B.* 7, 404) and chloro-di-nitro-phenol [81°].

Salts.—KA′ 2aq: flat monoclinic prisms; S. 10·8 at 20°; 44·3 at 100°.—KA′ aq.—KA′ (from alcohol): needles.—NaA′: groups of needles.—LiA′ aq.—NH_4A': [230°].—BaA'_2.—$BaC_6H_3ClSO_4$ 2aq.—CaA'_2 2aq: easily soluble needles.—MgA'_2 6aq: small flat plates or needles.—CuA'_2 6aq: greenish-white needles, v. e. sol. water.

Ethyl derivative $C_6H_3Cl(OEt)SO_3H$.

Salt.—KA′: stellate groups of needles.

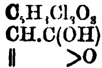
Chloro-phenol disulphonic acid $C_6H_2Cl(OH)(SO_3H)_2$ [4:1:6:2]. Formed, together with di-chloro-phenol sulphonic acid, by heating tri-chloro-phenol with K_2SO_3 at 170° (Armstrong a. Harrow, *C. J.* 29, 474). The same acid appears to be formed by sulphonating *p*-chloro-phenol at 100° (Petersen a. Baehr-Praderi, *A.* 157, 153). Conc. HNO_3 forms chloro-di-nitro-phenol [81°].

Di-chloro-phenol sulphonic acid $C_6H_2Cl_2(OH)(SO_3H)$ [4:2:1:6]. From (4,2,1)-di-chloro-phenol and $ClSO_3H$ [43°] (Armstrong, *C. J.* 25, 93). Formed also by chlorinating phenol *o*-sulphonic acid; and by heating tri-chloro-phenol with K_2SO_3 at 170° (Armstrong a. Harrow). HNO_3 (S.G. 1·36) forms di-chloro-nitro-phenol [121°].

Di-chloro-phenol sulphonic acid $C_6H_2Cl_2(OH)(SO_3H)$ [2:6:1:4]. Formed by chlorinating phenol *p*-sulphonic acid (Kolbe a. Gauhe, *A.* 147, 76) and by sulphonating (2,6,1)-di-chloro-phenol. Deliquescent trimetric tables or prisms. HNO_3 forms di-chloro-nitro-phenol and chloro-di-nitro-phenol [111°] (Faust, *Z.* 1871, 338; Armstrong, *C. J.* 24, 1112).—BaA'_2 2aq (dried at 100°).

Tri-chloro-phenol sulphonic acid $C_6HCl_3(OH)(SO_3H)$. From tri-chloro-phenol and $ClSO_3H$ (Armstrong, *C. J.* 25, 97; *cf.* Kekulé, *K.* 3, 233). Its aqueous solutions decompose with deposition of tri-chloro-phenol.

TRI-CHLORO-PHENOMALIC ACID $C_5H_3Cl_3O_3$ *i.e.* $CCl_3.CO.CH:CH.CO_2H$ or



$$\begin{array}{l}CH.C(OH).CCl_3\\ \| \qquad >O\\ CH.CO\end{array}$$

(Anschutz, *A.* 239, 176). *Tri-chloro-acetyl-acrylic acid.* [132°]. From benzene (80g.), H_2SO_4 (1,200 g.) and water (600 g.), to which $KClO_3$ (120 g.) is slowly (in 5 days) added with gentle shaking. The benzene is then separated and evaporated, the residue is extracted with water and the acid (6 g.) extracted from the water by ether (Carius, *A.* 140, 317; 142, 131; Kekulé a. O. Strecker, *A.* 223, 179). Quinone may be substituted for benzene.

Properties.—Glittering plates (from water). May be sublimed. Is volatile with steam.

Reactions.—1. Warmed with baryta it gives chloroform and baric maleate.—2. Combines with bromine in chloroform with formation of $CCl_3.CO.CHBr.CHBr.CO_2H$ [97·5°]. This is sl. sol. water, v. sol. alcohol, ether, and chloroform. Boiled with lime water, it gives chloroform and inactive calcic tartrate.

Theory of Formation.—Kekulé supposes that it is produced from chloro-quinone, and if this is written $CO\left\langle\begin{matrix}CH:CH\\CH:CCl\end{matrix}\right\rangle CO$ the conversion of it into $CO\left\langle\begin{matrix}CH:CH\\OH\ CCl_3\end{matrix}\right\rangle CO$ does not appear very difficult to understand.

CHLORO-PHENOXY-ACETIC ACID $C_8H_7ClO_3$ *i.e.* $C_6H_4Cl.O.CH_2.CC_2H$. [152°]. From phenoxy-acetic acid by successive treatment with PCl_5 and water (Michael, *J. pr.* [2] 35, 96). Trimetric prisms (from water).

o-**CHLORO-DIPHENYL** $C_{12}H_9Cl$ *i.e.* $C_6H_5.C_6H_4Cl$ [2:1]. [34°]. (267°). Formed, together with the *p*-isomeride, by passing chlorine into diphenyl mixed with $SbCl_5$ (Krämers, *A.* 189, 142). Monoclinic crystals; v. sol. ligroïn. CrO_3 gives *o*-chloro-benzoic acid.

m-**Chloro-diphenyl** $C_6H_5.C_6H_4Cl$ [3:1]? [89°]. Formed by heating C_6H_5OK with calcium *m*-chloro-benzoic acid (Pfannkuch, *J. pr.* [2] 6, 106).

p-**Chloro-diphenyl** $C_6H_5.C_6H_4Cl$ [4:1]. [75°]. (282°). Formed by chlorinating diphenyl (*v. supra*) or by treating *p*-oxy-diphenyl with PCl_5 (G. Schultz, *B.* 7, 52). Thin plates (from ligroin). Smells like oranges May be oxidised to *p*-chloro-benzoic acid.

Di-*p*-chloro-diphenyl [4:1]$C_6H_4Cl.C_6H_4Cl$[1:4]. [148°]. (c. 317° cor.).

Formation.—1. Amongst the products of the action of PCl_5 on di-*p*-oxy-diphenyl (Schmidt a. Schultz, *B.* 12, 494; *A.* 207, 339).—2. From di-amido-diphenyl (benzidine) by displacement of NH_2 by Cl through the diazo- reaction (Griess, *Tr.* 1864, iii. 730); *e.g.* by heating tetrazo-diphenyl with a large excess of HCl; the yield being 16 p.c. of the theoretical (Gasiorowski a. Wayss, *B.* 18, 1941).—3. By chlorinating diphenyl (Kramers, *A.* 189, 138, 145).—4. By passing chloro-benzene through a red-hot tube.

Properties. Prisms or needles; insol. water, sl. sol. alcohol, v. sol. ether. CrO_3 gives *p*-chloro-benzoic acid.

Penta-chloro-diphenyl $C_{12}H_5Cl_5$. [179°]. Formed together with other products by the action of PCl_5 on di-*p*-oxy-diphenyl (Schmidt a. Schultz, *B.* 12, 495; *cf.* Doebner, *B.* 9, 130). Long needles. Sublimable.

Per-chloro-diphenyl $C_{12}Cl_{10}$. Prepared by exhaustive chlorination of diphenyl in presence of $SbCl_5$ or iodine (Ruoff, *B.* 9, 1491; Weber a. Sollscher, *B.* 16, 882; Merz a. Weith, *B.* 16, 2881). Formed also by exhaustive chlorination of ditolyl (Merz a. Weith, *B.* 12, 677), benzidine, carbazole (Zetter, *B.* 10, 1233), and phenanthraquinone (Merz a. Weith, *B.* 16, 2871). Long tables or prisms. Does not melt below 270°. V. sl. sol. alcohol or ether. Not attacked by $SbCl_5$ even at 350°. Alcoholic NaOH at 150° gives $C_{12}Cl_8(OH)_2$.

α-**CHLORO-PHENYL-ACETIC ACID** $C_8H_7ClO_2$ *i.e.* $C_6H_5.CHCl.CO_2H$. [78°].

Formation.—1. From mandelic acid $C_6H_5.CH(OH).CO_2H$ and HCl at 140° (Radziszewski, *B.* 2, 208).—2. From benzoic aldehyde by conversion into PhCH(OH)CN by KCN and HCl, the mandelo-nitrile being then treated with HCl (Spiegel, *B.* 14, 235; R. Meyer, *A.* 220, 41). 3. From $C_6H_5.CH:CH.NO_2$ and fuming HCl at 100° (Priebs, *A.* 225, 337).

Properties.—Trimetric tables; sl. sol. cold water and ligroïn, v. e. sol. alcohol and ether. Sodium amalgam converts it into phenyl-acetic acid. Boiling aqueous KOH forms mandelic acid. Phenyl-hydrazine forms benzylidene-phenyl-hydrazine $C_6H_5CH:N_2HPh$ (Reissert, *B.* 17, 1452). The salts are unstable.

Methyl ether MeA′ (248° cor.). Oil (Meyer a. Boner, *B.* 14, 2392).

p-**Chloro-phenylacetic acid** $C_6H_4ClCH_2.CO_2H$. [104°]. Prepared by saponification of the nitrile (Neuhof, *A.* 147, 316; Jackson a. Field, *P. Am. A.* 14, 58). Also by treating phenyl-acetic acid with Cl in sunshine (Radziszewski, *B.* 2, 208). Long needles (from water). V. sol. benzene, water, alcohol, and ether.—AgA′: curdy mass.—CaA′$_2$ aq.

Amide $C_6H_4Cl.CH_2.CONH_2$. [175°]. Tables (from alcohol). V. sol. alcohol and ether, sl. sol. hot water.

Nitrile $C_6H_4Cl.CH_2.CN$. [29°]. From *p*-chloro-benzyl bromide by heating with alcoholic KCy (Jackson a. Field, *Am.* 2, 88). Prisms; sol. alcohol and ether.

Di-α-chloro-phenyl-acetic acid $C_6H_5.CCl_2.CO_2H$. [68°]. Prepared by the action of PCl_5 on phenyl-glyoxylic ether and subsequent saponification (Claisen, *B.* 12, 630). Small tables. V. sol water, alcohol, and ether.

Ethyl ether A′Et. (263°-266°).

Nitrile $C_6H_5.CCl_2.CN$. (224°). From benzoyl cyanide and PCl_5 (C.).

DI-α-CHLORO-PHENYL-ACETIC ALDEHYDE $C_6H_5.CCl_2.CHO$. (295°). From chloral, benzene, and Al_2Cl_6 at 70°. The product is treated with water and fractionally distilled *in vacuo*, when the compound $C_6H_5.CCl_2.CHCl(OH)$ passes over at 180°. By the action of KOH it is converted into the aldehyde by removal of HCl (Combes, *C. R.* 98, 678). Liquid. Reduces Fehling's solution and combines with $NaHSO_3$, although with difficulty. Benzene and Al_2Cl_6 convert the aldehyde into tri-phenyl-methane.

CHLORO-PHENYL-ACRYLIC ACID *v.* CHLORO-CINNAMIC ACID.

CHLORO-PHENYL-AMIDO-CHLORO-NAPHTHOQUINONE *v.* CHLORO-NAPHTHOQUINONE-CHLORO-ANILIDE.

CHLORO-PHENYL-AMIDO-HYDRONAPHTHOQUINONE $C_{16}H_{12}ClNO_2$ *i.e.* $C_{10}H_4Cl(OH)_2(NHPh)$. [171°]. From chloro-naphthoquinone anilide and conc. aqueous $SnCl_2$ (Knapp a. Schultz, *A.* 210, 190).

Acetyl derivative [169°].

CHLORO-DI-PHENYL-DI-AMIDO-HYDROQUINONE $C_{18}H_{15}ClN_2O_2$ *i.e.* $C_6HCl(OH)_2(NHPh)_2$. From chloro-di-phenyl-di-amido-quinone, conc. $SnCl_2$Aq, and alcohol (Knapp a. Schultz, *A.* 210, 181). Slender needles. Decomposes about 223°. Readily oxidised to the corresponding quinone.

Di-chloro-di-phenyl-di-amido-hydroquinone $C_{18}H_{14}Cl_2N_2O_2$ *i.e.* $C_6Cl_2(NHPh)_2(OH)_2$. Formed by boiling di-chloro-di-phenyl-di-amido-quinone $C_6Cl_2(NPhH)_2O_2$ with conc. aqueous $SnCl_2$ (Knapp a. Schultz, *A.* 210, 181). Slender needles, v. sol. water. Oxidation gives $C_6Cl_2(NPhH)_2O_2$. Boiling Ac_2O gives long needles of $C_{18}H_{20}N_2O_6$ [255°].

***p*-CHLORO-DI-PHENYL-DI-*p*-AMIDO-TRI-PHENYL-METHANE** $C_6H_4Cl.CH(C_6H_4.NHPh)_2$. Not isolated in a pure state. Formed by heating together diphenylamine and *p*-chloro-benzaldehyde in presence of $ZnCl_2$. On oxidation it gives a green dye-stuff (Kaeswurm, *B.* 19, 745).

TRI-CHLORO-TRI-PHENYL-TRI-AMIDO-DI-PHENYL-TOLYL-CARBINOL *v.* TRI-CHLORO-TRI-PHENYL-ROSANILINE.

CHLORO-PHENYL-AMIDO-QUINONES *v.* ANILIDES of CHLORO-QUINONES.

***p*-CHLORO-DI-PHENYL-AMINE** $PhNHC_6H_4Cl$. [74°]. Formed by treating diazotised *p*-amido-di-phenyl-amine with cuprous chloride (Ikuta, *A.* 248, 286). Long prisms. V. sl. sol. water, v. sol. ether, alcohol, benzene, petroleum ether. Yields a nitrosamine $PhN(NO)C_6H_4Cl$ [88°], v. sol. alcohol and ether, which on standing with alcoholic HCl is converted into the isomeric *p*-nitroso-chloro-di-phenyl-amine $C_6H_4(NO)NHC_6H_4Cl$ [159°] green plates (from benzene).

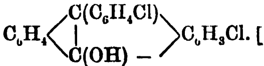
Di-chloro-di-phenyl-amine $NH(C_6H_4Cl)_2$. [80°]. From the benzoyl derivative and alcoholic KOH at 160° (Claus a. Schaare, *B.* 15, 1286). Needles.

Benzoyl derivative $NBz(C_6H_4Cl)_2$. [153°]. From benzoyl-di-phenyl-amine by chlorination (C. a. S.; *cf.* Claus, *B.* 14, 2368). Needles (from alcohol).

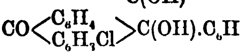
Tetra-chloro-di-phenyl-amine $NH(C_6H_3Cl_2)_2$. [134°]. Formed by passing Cl into a solution of di-phenyl-amine in HOAc (Gnehm, *B.* 8, 1040). Prisms or needles.

Per-chloro-tri-phenyl-amine $N(C_6Cl_5)_3$. From tri-phenyl-amine by exhaustive chlorination (Ruoff, *B.* 9, 1494). Needles (from benzene-alcohol).

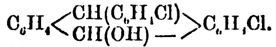
DI-CHLORO-PHENYL-ANTHRANOL



$C_{20}H_{12}Cl_2O$ *i.e.* $C_6H_4\left\langle\begin{matrix}C(C_6H_4Cl)\\ |\\ C(OH)\ -\end{matrix}\right\rangle C_6H_3Cl$. [170°].



From $CO\left\langle\begin{matrix}C_6H_4\\ C_6H_3Cl\end{matrix}\right\rangle C(OH).C_6H_4Cl$ (phenol-phthalidein chloride), acetic acid, and zinc-dust (Baeyer, *A.* 202, 95). Needles (from alcohol). V. sl. sol. alcohol; m. sol. acetone and ether, with bluish-green fluorescence.



Dihydride $C_6H_4\left\langle\begin{matrix}CH(C_6H_4Cl)\\ CH(OH)\ -\end{matrix}\right\rangle C_6H_3Cl$. *Hydrophenolphthalidin chloride.* [56°]. From the preceding by heating in alcoholic solution with sodium amalgam (B.). Long needles (from CS_2).

PER-CHLORO-DI-PHENYL-BENZENE $C_{18}Cl_{14}$. Formed by exhaustive chlorination of di-phenyl-benzene by means of $SbCl_5$ (Merz a. Weith, *B.* 16, 2881). Colourless needles. V. sol. hot nitrobenzene, sl. sol. alcohol, ether, and acetic acid.

Per-chloro-tri-phenyl-benzene $C_{24}Cl_{18}$. Formed by exhaustive chlorination of tri-phenyl-benzene by means of $SbCl_5$ (Merz a. Weith, *B.* 16, 2883). Colourless needles. V. sol. hot nitrobenzene, sl. sol. ether, benzene, and alcohol. It is only slightly attacked by HNO_3 at 350°.

CHLORO-PHENYL BENZYL OXIDE $C_6H_4Cl.O.CH_2Ph$. [71°]. From phenyl benzyl oxide and Cl in presence of HgO (Sintenis, *A.* 161, 338). Long needles (from alcohol).

TRI-CHLORO-DI-PHENYL-BUTANE $C_{16}H_{15}Cl_3$ *i.e.* $CH_3.CHCl.CCl_2.CHPh_2$. [80°]. S. (ether) 50; (alcohol) 2. From tri-chloro-butyric aldehyde, benzene, and H_2SO_4 (Hepp, *B.* 7, 1420). Monoclinic prisms (from ether-alcohol).

TRI-CHLORO-DI-PHENYL-BUTANE DISULPHONIC ACID $C_{16}H_{13}Cl_3(SO_3H)_2$. From $C_{16}H_{15}Cl_3$ and fuming H_2SO_4 (Hepp, *B.* 7, 1420).—BaA″.

CHLORO-DI-PHENYL-*tert*-BUTYL ALCOHOL $CClPh_2.CMe_2OH$. (239°). From liquid acetone-chloroform, benzene, and Al_2Cl_6 (Willgerodt, *J. pr.* [2] 37, 362).

Di-chloro-phenyl-*tert*-butyl alcohol $CCl_2Ph.CMe_2OH$. (217°). From acetone-chloroform, benzene, and Al_2Cl_6 (Willgerodt a. Genieser, *J. pr.* [2] 37, 367). Liquid.

CHLORO-*o*-PHENYLENE-DIAMINE $C_6H_7ClN_2$ *i.e.* $C_6H_3Cl(NH_2)_2$ [4:2:1]. [72°]. From chloro-di-nitro-benzene [39°] by reduction with tin and HCl (Laubenheimer, *B.* 9, 773). Laminæ. Fe_2Cl_6 gives a red colour and a brown pp.

Chloro-*m*-phenylene-diamine $C_6H_3Cl(NH_2)_2$ [4:3:1]. [86°]. From chloro-di-nitro-benzene [50°], tin, and HCl (Beilstein a. Kurbatoff, *A.* 197, 76). Needles (from ligroïn).

Chloro-*p*-phenylene-diamine $C_6H_3Cl(NH_2)_2$ [2:4:1]. [123·5°]. From di-chloro-nitro-aniline [188°], tin, and HCl (Witt, *B.* 8, 145). Flat needles.—B′HCl: long needles.

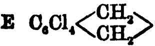
Di-chloro-*o*-phenylene-diamine $C_6H_2Cl_2(NH_2)_2$ [5:3:2:1]. [60·5°]. From di-chloro-nitro-aniline [100°], tin and HCl (Witt, *B.* 7, 1604). Long flexible needles (from alcohol).

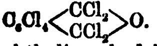
Di-chloro-*p*-phenylene-diamine $C_6H_2Cl_2(NH_2)_2$ [5:2:4:1]. [164°]. Formed, together with di-methyl-*p*-phenylene-diamine and di-chloro-di-methyl-*p*-phenylene-diamine, by boiling nitroso-di-methyl-aniline with HCl (S.G. 1·2) (Mohlau, *B.* 19, 2010). Colourless glistening prisms. By $K_2Cr_2O_7$ and H_2SO_4 it is oxidised to di-chloro-quinone [159°]. The dilute HCl solution on treatment with chloride of lime yields di-chloro-quinone-di-chlorimide [134°].

Tetra-chloro-*p*-phenylene diamine $C_6Cl_4(NH_2)_2$. [218°]. Formed by boiling quinone dichlorimide with HCl (S.G. 1·2) (Krause, *B.* 12, 51). Red needles (from dilute alcohol).

DI-CHLORO-DI-PHENYLENE KETONE $C_{13}H_6Cl_2O$. [158°]. From di-chloro-fluorene by CrO_3 (Hodgkinson a. Matthews, *C. J.* 43, 170).

DI-α-CHLORO-PHENYLENE-DI-METHYL-DI-MALONIC ETHER $C_6H_4(CH_2CCl(CO_2Et)_2)_2$. *v. Exo-di-chloro-xylylene-malonic ether.*

TETRA-CHLORO-PHENYLENE-DI-METHYL OXIDE  $C_6Cl_4{<}^{CH_2}_{CH_2}{>}O$. [218°]. V.D. 8·6 (calc. 8·9). From tetra-chloro-phthalic acid, HI, and P at 230° (Græbe, *A.* 238, 331). Needles (from benzene).

Octo-chloro-phenylene-di-methyl oxide  $C_6Cl_4{<}^{CCl_2}_{CCl_2}{>}O$. [140°]. From tetrachloro-phthalic anhydride and PCl_5 at 200° (G.)

DI-CHLORO-PHENYLENE-(α)-NAPHTHYLENE-OXIDE $C_{16}H_8Cl_2O$. [245°]. Prepared by the action of PCl_5 on phenylene-(α)-naphthylene-oxide (Arx, *B.* 13, 1727). Fine white needles. V. sol. alcohol and ether, sl. sol. benzene.

TETRA-CHLORO-PHENYLENE OXIDE C_6Cl_4O (?) [320°]. (above 360°). Formed by distilling potassium penta-chloro-phenol C_6Cl_5OK (Merz a. Weith, *B.* 5, 461). Flat needles. V. sl. sol. alcohol and ether. Not affected by PCl_5 at 250° or by sodium-amalgam.

CHLORO-PHENYL-ETHANE *v.* CHLORO-ETHYL-BENZENE.

Chloro-di-phenyl-ethane $C_{14}H_{13}Cl$ *i.e.* $CH_2Cl.CHPh_2$. From di-chloro-di-ethyl oxide $CH_2Cl.CHCl.OEt$, benzene, and H_2SO_4 (Hepp, *B.* 6, 1439). Liquid. Splits up on distillation or treatment with alcoholic KOH into HCl and $C_{14}H_{12}$.

Di-*p*-chloro-di-phenyl-ethane $C_6H_4Cl.CH_2.CH_2.C_6H_4Cl$. *Di-chloro-dibenzyl.* [112°]. Formed by passing chlorine over a solid cake of dibenzyl (150 pts.) and iodine (1 pt.) till the cake liquefies. This is distilled and the product crystallised from alcohol (Kade, *J. pr.* [2] 19, 462). Glittering plates which feel greasy. Sol. alcohol, ether, and chloroform. Chromic mixture oxidises it to *p*-chloro-benzoic acid.

(α)-Di-*exo*-chloro-*s*-di-phenyl ethane $C_6H_5.CHCl.CHCl.C_6H_5$. *Stilbene (α)-chloride.* [193°]. Formed, together with the (β)-isomeride, by the action of PCl_5 on hydrobenzoïn (Zincke, *A.* 198, 129) and by the union of Cl with *s*-di-phenyl-ethylene (Laurent, *B. J.* 25, 620). Formed also from isohydrobenzoin and PCl_5 (Ammann, *A.* 168, 67). Perhaps identical with the compound [180°] which is formed by heating benzylidene chloride with copper-powder at 100° (Onufrowicz, *B.* 17, 835).

Properties.—Silky needles (from alcohol), prisms (from toluene), or plates (O.). Sl. sol. boiling alcohol. May be sublimed. Alcoholic KOH forms *s*-di-phenyl-acetylene (tolane). AgOAc followed by KOH gives isohydrobenzoin.

(β)-Di-*exo*-chloro-*s*-di-phenyl-ethane $C_6H_5.CHCl.CHCl.C_6H_5$. *Stilbene (β)-chloride.* [94°]. Formed as above. Thick tables. At 200° it is partially converted into the (α)-isomeride.

Tri-chloro-*s*-di-phenyl-ethane $C_{14}H_{11}Cl_3$. [85°]. From *s*-di-phenyl-ethylene and Cl (Laurent).

Tri-chloro-*u*-di-phenyl-ethane $CCl_3.CHPh_2$. [64°]. From chloral, benzene, and H_2SO_4 (Baeyer, *B.* 5, 1098). Small thin plates. Alcoholic KOH gives $CPh_2:CCl_2$.

Tri-chloro-*u*-di-phenyl-ethane $CH_2Cl.CH(C_6H_4Cl)_2$. From di-chloro-di-ethyl-oxide $CH_2Cl.CHCl.OEt$, chloro-benzene, and H_2SO_4 (Hepp, *B.* 7, 1419). On distillation it gives $CH_2:C(C_6H_4Cl)_2$.

Tetra-chloro-*s*-di-phenyl-ethane $C_6H_5.CCl_2.CCl_2.C_6H_5$. *Tolane tetra-chloride.* [163°].

Formation.—1. From benzil and PCl_5 (Zinin, *Z.* 1868, 718).—2. A by-product in the preparation of benzotrichloride by chlorinating toluene (Liebermann a. Homeyer, *B.* 12, 1971). 3. By heating benzotrichloride with copper-powder at 100° (Onufrowicz, *B.* 17, 833).—4. By heating benzotrichloride with benzene and copper-powder (Hanhart, *B.* 15, 901).

Properties.—Trimetric crystals; sol. benzene, hot alcohol, and ether. Gives a violet dye with dimethylaniline and $ZnCl_2$. Alcohol and zinc-dust gives (α) and (β) di-chloro-di-phenyl-ethylene.

Penta-chloro-*u*-di-phenyl-ethane $CCl_3.CH(C_6H_4Cl)_2$. [105°]. S. (95 p.c. alcohol) 10. From chloral, chlorobenzene, and H_2SO_4 (Zeidler, *B.* 7, 1181). Felted needles (from ether-alcohol). Alcoholic KOH gives $C_{14}H_8Cl_4$.

CHLORO-DI-PHENYL-ETHYLENE $C_6H_5.CCl:CH.C_6H_5$. *Chloro-stilbene.* From stilbene di-chloride and alcoholic KOH (Zinin, *A.* 149, 375). Oil.

(α)-Di-chloro-*s*-di-phenyl-ethylene $C_6H_5.CCl:CCl.C_6H_5$. *Tolane-(α)-di-chloride.* [143°]. Formed, together with the (β)-modification, by the action of powdered zinc on an alcoholic solution of tetra-chloro-di-phenyl ethane (Liebermann a. Homeyer, *B.* 12, 1973; *cf.* Zinin, *B.* 4, 289); or of iron powder on an acetic acid solution of the same body (Lachowicz, *B.* 17, 1165). Formed also by passing Cl into a solution of *s*-di-phenyl-ethylene in chloroform. Both modifications are also formed by heating benzo-trichloride with copper-powder (Hanhart, *B.* 15, 899), and by heating *s*-di-phenyl-ethylene with PCl_5 at 180° (Limpricht a. Schwanert, *B.* 4, 379). Trimetric tables or prisms. Sl sol. alcohol. Alcoholic KOH at 180° gives *s*-di-phenyl-acetylene (tolane).

(β)-Di-chloro-*s*-di-phenyl-ethylene $C_6H_5.CCl:CCl.C_6H_5$. *Tolane-(β)-di-chloride.* [63°]. Formed as above. Long needles. More soluble in alcohol than the (α)-modification. The (α) and (β) modifications can be partially changed into one another by distillation.

Di-chloro-*u*-di-phenyl-ethylene $CCl_2:CPh_2$. [80°]. Formed by passing Cl into *u*-di-phenyl-ethylene and distilling the resulting $CCl_3.CClPh_2$ (Hepp). Formed also from $CCl_3.CHPh_2$ by boiling with alcoholic KOH (Baeyer, *B.* 6, 223). Monoclinic prisms (from alcohol).

Di-chloro-di-phenyl-ethylene $C_6H_4Cl.CH:CH.C_6H_4Cl$. [170°]. Formed by passing Cl in excess into melted dibenzyl (Kade, *J. pr.* [2] 19, 466). Needles or plates (from alcohol).

Di-chloro-*u*-di-phenyl-ethylene $CH_2:C(C_6H_4Cl)_2$. (283°). Formed by distilling $CH_2Cl.CH(C_6H_4Cl)_2$ (Hepp, *B.* 7, 1419).

Tri-chloro-*s*-di-phenyl-ethylene $C_{14}H_9Cl_3$. Two modifications are formed by treating *s*-di-phenyl-acetylene (tolane) with PCl_5 (Limpricht a. Schwanert, *B.* 4, 379).

(α)-Modification: [137°-145°]; needles.

(β)-Modification: [150°]; prisms.

Tetra-chloro-di-phenyl-ethylene $CCl_2:C(C_6H_4Cl)_2$. [89°]. From $CCl_3.CH(C_6H_4Cl)_2$ and alcoholic KOH (Zeidler, *B.* 7, 1181).

ω-TRI-CHLORO-DI-PHENYL-ETHYLIDENE DIAMINE $C_{14}H_{13}N_2Cl_3$ *i.e.* $CCl_3.CH(NHC_6H_5)_2$. [101°]. Formed by the action of aniline on chloral (Wallach, *B.* 5, 251; *A.* 173, 277). Tabular crystals (from alcohol). Insol. water. Decomposes at 150°. Boiling with alkalis forms phenyl carbamine.—$B'_2H_2PtCl_6$ (Amato, *B.* 9, 198).

DI-CHLORO-DI-PHENYL-GUANIDINE $C_{13}H_{11}Cl_2N_3$ *i.e.* $NH:C(NH.C_6H_4Cl)_2$. From aqueous di-phenyl-guanidine hydrochloride and Cl (Hofmann, *A.* 67, 147). Laminæ (from alcohol). $B'_2H_2PtCl_6$.

Di-chloro-di-phenyl-guanidine $NH:C(NH.C_6H_4Cl)_2$. [141°]. From di-chloro-di-phenyl-thio-urea, PbO, and NH_3 (Losanitsch, *Bl.* [2] 32, 170). Needles. Perhaps identical with the preceding.

Tri-*p*-chloro-tri-phenyl-guanidine $C_{19}H_{14}Cl_3N_3$ *i.e.* $C_6H_4Cl.N.C(NH.C_6H_4Cl)_2$. Formed by adding iodine to an alcoholic solution of di-chloro-di-phenyl-thio-urea $CS(NH.C_6H_4Cl)_2$ (Beilstein a. Kurbatoff, *A.* 176, 51). Slender needles (from CS_2). —B'HCl.—B'HI: [255°].—$B'_2H_2SO_4$.

CHLORO-DI-PHENYL-KETONE *v.* CHLORO-BENZOPHENONE.

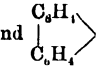
CHLORO-PHENYL MERCAPTAN $C_6H_4Cl.SH$. [54°]. From chloro-benzene sulphonic chloride, zinc, and dilute H_2SO_4 (Otto, *A.* 143, 109). Four-sided trimetric tables (from alcohol).—$(C_6H_4Cl.S)_2Pb$: yellow pp.

***p*-CHLORO-PHENYL MERCAPTURIC ACID** $C_{11}H_{12}ClNSO_3$ *i.e.* $CH_3.CO.NH.CMe(S.C_6H_4Cl).CO_2H$. [154°]. Found in the urine of a dog after it had taken chloro benzene (Jaffé, *B.* 12, 1092). Colourless leaflets or tables. V. sl. sol. ether, v. sol. alcohol.

β-CHLORO-β-PHENYL-METHACRYLIC ACID $C_{10}H_9ClO_2$ *i.e.* $C_6H_5.CCl:CMe.CO_2H$. [116°]. From methyl-benzoyl-acetic ether, $POCl_3$, and PCl_5 (Perkin, jun., a. Calman, *C. J.* 49, 159). Needles, v. sol. alcohol, ether, benzene, and HOAc, m. sol. cold light petroleum.—AgA'.

CHLORO-DI-PHENYL-METHANE $(C_6H_5)_2CHCl$. *Di-phenyl-carbinyl chloride.* [14°] From di-phenyl-carbinol and HCl (Engler a. Bethge, *B.* 7, 1128). Decomposed by heat into HCl, tetra-phenyl-ethylene, and tetra-phenyl-ethane (Anschutz, *A.* 235, 220).

Di-chloro-di-phenyl-methane $(C_6H_5)_2CCl_2$. *Benzophenone chloride.* (305° i.V.). S.G. $\frac{18}{}$ 1·235. From benzophenone and PCl_5 (Behr, *B.* 3, 752). Liquid. Decomposed by distillation. Warm water reconverts it into benzophenone. KHS gives $(C_6H_5)_2CS$. Heating with silver forms $Ph_2C.CPh_2$. Aniline forms $Ph_2C:NPh$. Di-methyl-aniline gives $Ph_2CH.C_6H_4NMe_2$ (Pauly, *A.* 187, 198).

Chloro-tri-phenyl-methane $(C_6H_5)_3CCl$. *Tri-phenyl carbinyl chloride.* [105°-115°]. From tri-phenyl-carbinol and PCl_5 (Hemilian, *B.* 7, 1207). Formed also by the action of benzene on CCl_4 in presence of Al_2Cl_6 (Friedel a. Crafts, *A. Ch.* [6] 1, 502). At 250° it gives HCl, tri-phenyl-methane, and  $\left.\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\right>CH.C_6H_5$ (Hemilian, *B.* 11, 837). Hot water forms tri-phenyl-carbinol.

DI-CHLORO-TRI-PHENYL-METHANE CARBOXYLIC ACID $(C_6H_4Cl)_2CH.C_6H_4.CO_2H$. [206°]. From di-chloro-di-phenyl-phthalide and boiling alcoholic NaOH; the resulting $(C_6H_4Cl)_2C(OH).C_6H_4.CO_2H$ being reduced with zinc-dust and aqueous NaOH (Baeyer, *A.* 202, 84). Six-sided tables (from alcohol). CrO_3 gives di-chloro-phenyl-oxanthranol.

Tetra-chloro-di-phenyl-methane carboxylic acid *v.* TETRA-CHLORO-*o*-BENZYL-BENZOIC ACID.

DI-CHLORO-DI-PHENYL-METHANE SULPHONIC CHLORIDE $C_{13}H_8S_2O_4Cl_4$ *i.e.* $CCl_2(C_6H_4SO_2Cl)_2$. [129°]. From $CO(C_6H_4SO_2Cl)_2$ and PCl_5 (Beckmann, *B.* 8, 992). Amorphous; sl. sol. alcohol.

TETRA-CHLORO-DI-PHENYL-METHYL-AMINE $C_{13}H_9NCl_4$ *i.e.* $(C_6H_3Cl_2)_2NMe$. [97°]. Formed by passing Cl into a solution of NPh_2Me in HOAc (Gnehm, *B.* 8, 1040). Prisms.

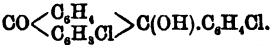
CHLORO-PHENYL-METHYL-KETONE *v.* CHLORO-ACETOPHENONE.

DI-CHLORO-PHENYL-OXAMIC ACID $C_6H_3Cl_2.NH.CO.CO_2H$. [122°]. S. ·124 at 25°. Prepared by boiling tetra-chloro-oxanilide (4 gr.), alcohol (125 cc.) and KHO (5 gr.) for 10 minutes (Dyer a. Mixter, *Am.* 8, 354). White fibres. Sol. alcohol and ether. KHO solution gives di-chloro-aniline [63°].

Salts.—KA': white hair-like fibres.

TETRA-CHLORO-DI PHENYL-OXAMIDE $C_2O_2(NH.C_6H_3Cl_2)_2$ [1:2:4]. *Tetra-chloro-oxanilide.* [c. 255°]. From oxanilide by chlorination in HOAc (Dyer a. Mixter, *Am.* 8, 349). White fibres.

DI-CHLORO-PHENYL OXANTHRANOL

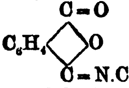
$C_{20}H_{12}Cl_2O_2$ *i.e.* 
$CO<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_3Cl}>C(OH).C_6H_4Cl$.
Phenol-phthalideïn-chloride. [156°]. From di-oxy-phenyl-oxanthranol (phenol - phthalideïn) and PCl_5 at 120° (Baeyer, *A.* 202, 100). Silky needles (from alcohol).

CHLORO-PHENYL-PHOSPHORIC ACID

$C_6H_6ClPO_4$ *i.e.* $C_6H_4ClO.PO(OH)_2$. [81°]. Formed together with *p*-di-chloro-benzene by treatment of phenol *p*-sulphonic acid and PCl_5; the resulting $C_6H_4Cl.O.POCl_2$ being decomposed by water (Kekulé, *B.* 5, 877; 6, 944).—BaA″.

Chloride $C_6H_4Cl.O.POCl_2$. (265°).

p-CHLOROPHENYL PHTHALIMIDE



[194°-195° uncor.]. Prepared by heating *p*-chloro-aniline with phthalic anhydride (Gabriel, *B.* 11, 2260). Long fine needles. Sol. hot alcohol, C_6H_6, and acetic acid.

α-CHLORO-α-PHENYL-PROPIONIC ACID

$C_9H_9ClO_2$ *i.e.* $CH_3.CClPh.CO_2H$. *Chloro-hydro-atropic acid* [73°]. From atrolactic acid and HCl in the cold (Merling, *A.* 209, 19). Small prisms, m. sol. hot water, sl. sol. cold water. Volatile with steam. Attacks the mucous membrane. Decomposes at 110°. Boiling alkaline carbonates form no styrene.

β-Chloro-α-phenyl-propionic acid

$CH_2Cl.CHPh.CO_2H$. *Chloro-hydratropic acid.* [89°]. Possibly identical with the preceding. Prepared by the action of HCl on the cyan-hydrin obtained from acetophenone and HCN (Spiegel, *B.* 14, 235). From tropic acid and PCl_5 followed by water (Ladenburg, *A.* 217, 77). Formed also by the union of atropic acid with fuming HCl at 100° (Merling, *A.* 209, 3). Colourless prisms. Sol. alcohol, ether, and benzene, sl. sol. water and ligroin. On boiling with aqueous NaOH it gives atropic acid. On heating with Na_2CO_3 solution to 130° tropic acid is formed. Boiling aqueous Na_2CO_3 forms tropic acid and a little styrene.

o-Chloro-β-phenyl-propionic acid

$C_6H_4Cl.C_2H_4.CO_2H$. *o-Chloro-hydrocinnamic acid.* [97°]. Needles or plates. Formed by reduction of *o*-chloro-cinnamic acid with HI and P (Gabriel a. Herzberg, *B.* 16, 2037).

m-Chloro-β-phenyl-propionic acid

$C_6H_4Cl.C_2H_4.CO_2H$. *m - Chloro - hydrocinnamic acid.* [78°]. White easily soluble plates. Formed by reduction of *m*-chloro-cinnamic acid with HI and P (G. a. H.).

p-Chloro-phenyl-propionic acid

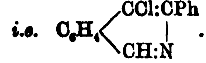
$C_6H_4Cl.C_2H_4.CO_2H$. *p-Chloro-hydrocinnamic acid* [124°]. Formed by reduction of *p*-chloro-cinnamic acid (G. a. H.).

β-Chloro-β-phenyl-propionic acid

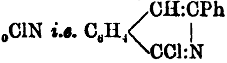
$C_6H_5.CHCl.CH_2.CO_2H$. [126°]. From β-oxy-β-phenyl-propionic acid and fuming HCl (Glaser, *A.* 147, 95). Very slowly formed by combination of cinnamic acid with HCl in conc. aqueous solution (Erlenmeyer, *B.* 14, 1867). Laminæ. Split up by heat into HCl and cinnamic acid; and by aqueous Na_2CO_3 into CO_2, HCl, and styrene.

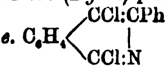
αβ-Di-chloro-β-phenyl-propionic acid

$C_6H_5.CHCl.CHCl.CO_2H$. [164°]. White plates. Formed by leading Cl into a CS_2 solution of cinnamic acid. With aqueous Na_2CO_3 it gives α-chloro-styrene (Erlenmeyer, *B.* 14, 1867).

(*Py.* 1)-CHLORO-(*Py.* 2)-PHENYL-ISOQUINOLINE $C_{15}H_{10}ClN$ *i.e.*  . [70°]. Obtained by reduction of (*Py.* 1:4)-di-chloro-(*Py.* 2)-phenyl-isoquinoline with HI and P. Glistening pillars. Salts.—B′HCl: small thick crystals.—$B'_2H_2Cl_2PtCl_4$: orange yellow needles (Gabriel, *B.* 18, 3475).

(*Py.* 4)-Chloro-(*Py.* 2)-phenyl-isoquinoline

$C_{15}H_{10}ClN$ *i.e.*  . [78°]. Prepared by boiling (*Py.* 4)-oxy-(*Py.* 2)-phenyl-isoquinoline (isobenzalphthalimidine) with $POCl_3$ (2 pts.). It is also formed by heating the same compound with PCl_5 at 100°-130°. Flat pointed needles. Sol. alcohol, v. sol. benzene, ether, petroleum-spirit, chloroform, and CS_2, insol. water. Heated with HI and P at 170° it is reduced to phenyl-isoquinoline (Gabriel, *B.* 18, 3473).

(*Py.* 1:4)-Di-chloro-(*Py.* 2)-phenyl-isoquinoline $C_{15}H_9Cl_2N$ *i.e.*  [163°]. Obtained by heating (*Py.* 4)-oxy-(*Py.* 2)-phenyl-isoquinoline (isobenzalphthalimidine) with PCl_5 at 100°. By boiling with HI and P it is reduced to (*Py.* 1)-chloro-(*Py.* 2)-phenyl-isoquinoline [70°] (Gabriel, *B.* 18, 3473).

TRI-CHLORO-TRI-PHENYL-ROSANILINE

$C_6H_4Cl.NH.C_6H_3Me.C(OH)(C_6H_4.NH.C_6H_4Cl)_2$. The *o*-, *m*- and *p*-compounds are formed by heating rosaniline with *o*-, *m*-, or *p*-chloraniline in presence of benzoic acid. They dye silk various shades of bluish violet (Heumann a. Heidlberg, *B.* 19, 1992).

DI-CHLORO-DI-PHENYL SULPHIDE

$(C_6H_4Cl)_2S$. [89°]. From 'thio-aniline' $S(C_6H_4NH_2)_2$ by displacement of NH_2 by Cl through the diazo- reaction (Krafft, *B.* 7, 1165).

Di-chloro-di-phenyl di-sulphide $(C_6H_4Cl)_2S_2$. [71°]. From $C_6H_4Cl.SH$ and HNO_3 (S.G. 1·12) (Otto, *A.* 143, 111). Tables. Zinc and dilute H_2SO_4 reconvert it into chloro-phenyl mercaptan.

CHLORO-DI-PHENYL SULPHONE

$C_6H_5.SO_2.C_6H_4Cl$. [92°]. (389°). From benzene sulphonic chloride, benzene, and Al_2Cl_6; the yield is 87 p.c. of the theoretical (Beckurts a. Otto, *B.* 11, 2067; 19, 2418). Leaflets. Insol. water; v. sol. hot alcohol.

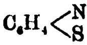
Di-o-chloro-di-phenyl sulphone $(C_6H_4Cl)_2SO_2$. [174°]. (360°). Formed in sulphonating *o*-di-chloro-benzene (Friedel a. Crafts, *A. Ch.* [6] 10, 414). Crystals.

Di-chloro-di-phenyl-sulphone $C_{12}H_8Cl_2SO_2$. (above 300°). Formed by chlorinating di-phenyl-sulphone in diffused daylight at 100° in presence of iodine (Otto a. Gruber, *A.* 149, 180). Oil.

Di-p-chloro-di-phenyl-sulphone $(C_6H_4Cl)_2SO_2$. [141°] (O.); [147°] (B. a. O.). From chloro-benzene and SO_3 (Otto, *A.* 145, 28). Also from chloro-benzene and $ClSO_3H$ (Beckurts a. Otto, *B.* 11, 2065). Plates. H_2SO_4 at 150° gives chloro-benzene sulphonic acid. Sodium amalgam in alcoholic solution gives benzene, chloro-benzene sulphonic acid, and benzene sulphonic acid.

CHLORO-PHENYL-THIO-CARBAMIC ETHER $C_6H_4Cl.NHCS.OEt$. [103°]. Formed by adding iodine to an alcoholic solution of di-chloro-di-phenyl-thio-urea (Beilstein a. Kurbatoff, *A.* 176, 52). Needles.

o-**CHLORO-PHENYL-THIO-CARBIMIDE** $C_6H_4(Cl).NCS$ [1:2]. [45°]. (250°). Crystalline solid. Prepared by the action of P_2O_5 on the corresponding urea derived from *o*-chloro-nitro-benzene (Hofmann, *B.* 13, 14). An isomeride is chloro-methenyl-amido-phenyl-mercaptan



$C_6H_4\left<\begin{matrix}N\\S\end{matrix}\right>CCl$.

m-**Chloro-phenyl-thiocarbimide** $C_6H_4(Cl).NCS$ [1:3]. (250°). Prepared by the action of P_2O_5 on the corresponding urea [122°] obtained from *m*-chloro-aniline and CS_2 (Hofmann, *B.* 13, 13). Liquid.

p-**Chloro-phenyl-thio-carbimide** $C_6H_4(Cl).NCS$ [1:4]. [45°]. (250°). Crystalline solid. Prepared by the action of CS_2 on *p*-chloro-aniline and decomposition of the resulting di-chloro-phenyl-urea (Hofmann, *B.* 13, 13; Beilstein a. Kurbatoff, *A.* 176, 51; Losanitsch, *B.* 5, 156).

DI-*o*-CHLORO-DI-PHENYL-THIO-UREA $C_{13}H_{10}Cl_2N_2S$ *i.e.* $CS(NH.C_6H_4Cl)_2$. [116°]. From *o*-chloro-aniline and CS_2 (Hofmann, *B.* 13, 14).

Di-*m*-chloro-di-phenyl-thio-urea [122°] (H.).

Di-*p*-chloro-di-phenyl-thio-urea [168°]. S. (in CS_2) ·0264 at 13·7° (Beilstein, *A.* 176, 47). From *p*-chloro-aniline, CS_2, and alcohol (Losanitsch, *B.* 5, 156; *Bl.* [2] 32, 170). Iodine acting on its alcoholic solution forms di-chloro-di-phenyl-urea, tri-chloro-tri-phenyl-guanidine, chloro-phenyl thio-carbimide, and chloro-phenyl-carbamic ether.

TRI-CHLORO-PHENYL-TOLYL-ETHANE CARBOXYIC ACID $C_{16}H_{13}Cl_3O_2$ *i.e.* $CH_3.C_6H_4.CH(CCl_3).C_6H_4.CO_2H$. [174°]. From $(CH_3.C_6H_4)_2CH.CCl_3$ and chromic mixture (O. Fischer, *B.* 7, 1192). Tables (from alcohol). Alkalis give $CH_3.C_6H_4C(CCl_2).C_6H_4.CO_2H$.

DI-CHLORO-PHENYL-TOLYL-KETONE CARBOXYLIC ACID *v.* Di-chloro-toluyl-benzoic acid.

ω-**CHLORO-PHENYL-TOLYL-METHANE** $CH_2Cl.C_6H_4.CH_2.C_6H_5$. A mixture of the *o*- and *p*- varieties of this body is one of the products of the action of benzyl chloride on water at a high temperature, the reaction being as follows: $2C_6H_5.CH_2Cl = HCl + CH_2Cl.C_6H_4.CH_2.C_6H_5$. The mixture on oxidation gives *o*- and *p*-benzoyl-benzoic acid (Senff, *A.* 220, 249).

DI-*p*-CHLORO-DI-PHENYL-UREA $(C_6H_4Cl.NH)_2CO$. A secondary product in the preparation of *p*-chloro-phenyl thiocarbimide by the action of P_2O_5 or of iodine on the corresponding thio-urea (Beilstein a. Kurbatoff, *A.* 176, 46). Long needles (from HOAc). Volatilises at 270°.

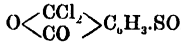
TRI-CHLORO-PHLOROGLUCIN $C_6H_3Cl_3O_3$. [129°]. Formed by passing chlorine into a solution of phloroglucin in HOAc until the liquid ceases to give a red colour with wood (Webster, *C. J.* 47, 423; Hazura a. Benedikt, *M.* 6, 706). Slender needles (containing 3aq). Dilute HNO_3 gives oxalic acid. Chlorine, in presence of CCl_4, gives chlorinated acetic aldehyde and tri-chloro-acetic acid. When chlorine is passed into an aqueous solution of phloroglucin there is formed di-chloro-acetic acid.

Hexa-Hydride $C_6H_9Cl_3O_3$. [125°]. From hexa-bromo-phloroglucin dibromide, tin, and HCl (H. a. B.). Needles (containing 3aq).

CHLORO-PHLORONE *v.* Chloro-xyloquinone.

u-**CHLORO-PHTHALIC ACID** $C_8H_5ClO_4$ *i.e.* $C_6H_3Cl(CO_2H)_2$ [4:2:1]. [148°] (C. a. D.; G. a. R.; C. a. M.); [130°] (I.); [c. 134°] (K.).

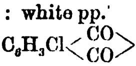
Formation.—1. By oxidation of (ε)-di-chloro-naphthalene [135°] (Alén, *Bl.* [2] 36, 434), of chloro-(β)-naphthol (Claus a. Dehne, *B.* 15, 320), of the two chloro-toluic acids [130°] and [166°] (Kruger, *B.* 18, 1758), of ('β')-di-chloro-(α)-naphthoquinone (Claus a. Müller, *B.* 18, 3076), and of chloro-di-ethyl-benzene (Istrati, *A. Ch.* [6] 6, 413).—2. By saponifying the chloride which may be formed by the action of PCl_5 on the tri-chloride of sulpho-phthalic acid



$O\left<\begin{matrix}CCl_2\\CO\end{matrix}\right>C_6H_3.SO_2Cl$ (Rée, *A.* 233, 236).

Properties.—Small needles. V. sol. water and alcohol; m. sol. dilute HCl, chloroform, and CS_2, sl. sol. benzene, insol. ligroin. With resorcin it gives a chloro-fluorescein.

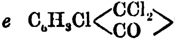
Salts.—K_2A'': large needles, v. sol. water.—BaA'': amorphous; sl. sol. water.—$BaH_2A''_2$: small needles, sl. sol. water.—CaA'': scales, sl. sol. water.—Ag_2A'': white pp.



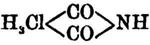
Anhydride $C_6H_3Cl\left<\begin{matrix}CO\\CO\end{matrix}\right>O$. [95°] (C. a. D.); [97°] (G. a. R.; K.); [114°] (I.). Formed by heating the acid. Triclinic needles (by sublimation).

Methyl ether Me_2A''. [37°]. Needles.

Ethyl ether Et_2A''. [−20°]. (c. 303°) (Graebe a. Rée, *C. J.* 49, 528).



Chloride $C_6H_3Cl\left<\begin{matrix}CCl_2\\CO\end{matrix}\right>O$. (276° uncor.). Liquid.



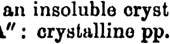
Imide $C_6H_3Cl\left<\begin{matrix}CO\\CO\end{matrix}\right>NH$. [211°]. From the anhydride and NH_3 (Rée, *A.* 233, 236).

c-**Chloro-phthalic acid** $C_5H_3Cl(CO_2H)_2$ [3:2:1]. [184°] (G.); [181°] (K.). S. 2·16 at 14°.

Formation. 1. By oxidation of chloro-toluic acid [154°] with $KMnO_4$ (Krüger, *B.* 18, 1758).—2. By oxidation of (γ)-di-chloro-naphthalene [107°] with CrO_3 in HOAc (Guareschi, *G.* 17, 121; *B.* 19, 131).

Properties.—Long needles; sl. sol. cold, v. sol hot, water; v. sol. alcohol and ether. Gives the anhydride on melting. Heated with phenol and conc. H_2SO_4 it gives a phthaleïn which dissolves in alkalis forming a violet solution.

Salts.—BaA''aq: long silky needles, v. sol. cold, sl. sol. hot, water. By boiling with water it is converted into an insoluble crystalline powder BaA''aq.—Ag_2A'': crystalline pp.



Anhydride $C_6H_3Cl\left<\begin{matrix}CO\\CO\end{matrix}\right>O$. [123°]. Needles (by sublimation). By chlorination of phthalic acid Auerbach (*J.* 1880, 862) obtained an (impure?) phthalic acid [150°] whose anhydride melted at 143°.

Di-chloro-phthalic acid $C_6H_2Cl_2(CO_2H)_2$. Formed by oxidation of the tri-chloro-naphthalene [90°] (from (β)-naphthol-(β)-di-sulphonate and PCl_5), by heating with dilute HNO_3 (S.G. 1·16) at 210°. Syrup. Could not be obtained crystallised although apparently pure.

Salts.—The Na and K salts are excessively

sol. water.—$A''Ba$: v. sol. amorphous solid.—$A''Ag_2$: white pp., nearly insol. cold water.—$A''Pb$: insol. white pp. (Claus a. Schmidt, *B.* 19, 3175).

(β)-Di-chloro-phthalic acid $C_6Cl_2H_2(CO_2H)_2$. [118°]. Formed by oxidation of a chlorinated naphthalene (Graebe a. Le Royer, *A.* 238, 350). V. e. sol. hot water, m. sol. cold water or alcohol.

Salts.—$(NH_4)_2A''$.—Ag_2A''.—CaA'' 4aq.—BaA'' 2aq.

Ethers.—Et_2A'' [60°].—$EtHA''$ [75°–85°].—$Et(NH_4)A''$.

Anhydride $C_6Cl_2H_2C_2O_3$. [c. 151°]. (340°).

Chloride $C_6Cl_2H_2C_2O_2Cl_2$. [below 50°]. (c. 314°).

Tetrachloride $C_6Cl_2H_2C_2OCl_4$. [117°]. (above 300°).

Imide $C_6Cl_2H_2C_2O_2NH$. [191°]. Reduced by Zn and HCl to dichlorophthalimidine [210°].

Di-chloro-phthalic acid $C_6H_2Cl_2(CO_2H)_2$. [183°]. Formed by oxidation of the di-chloro-*o*-xylene [4°] by dilute HNO_3 (Claus a. Kautz, *B.* 18, 1370). Formed also by oxidation of ('β')-di-chloro-naphthalene (Atterberg, *B.* 10, 547); and by boiling di-chloro-naphthalene tetrachloride with HNO_3 (Faust, *A.* 160, 64). Prisms; v. sol. hot water, alcohol, and ether.

Salts.—BaA'' aq.—CaA'' 4aq: prisms, sl. sol. water.

Anhydride $C_6H_2Cl_2C_2O_3$. [187°].

Tri-chloro-phthalic acid $C_6HCl_3(CO_2H)_2$. Formed by oxidation of tri-chloro-*o*-xylene [93°] by dilute HNO_3 (Claus a. Kautz, *B.* 18, 1370). Formed also by the action of conc. HNO_3 on (β)-penta-chloro-naphthalene (Atterberg a. Widmann, *B.* 10, 1841). Yellowish-white mass; converted by heat into the anhydride.

Anhydride [157°]. Needles.

Tetra-chloro-phthalic acid $C_6Cl_4(CO_2H)_2$. [250°]. S. ·57 at 14°; 3·03 at 99°.

Formation.—1. From (α)-penta-chloro-naphthalene and dilute HNO_3 at 190° (Graebe, *A.* 149, 18).—2. Together with penta-chloro-(α)-naphthoquinone, by oxidation of hepta-chloronaphthalene [194°] with HNO_3 (1·5 S.G.) at 100° (Claus a. Wenzlik, *B.* 19, 1166).

Preparation.—Phthalic anhydride (5 kilos.) is heated with $SbCl_3$ (30 kilos.) at 200°, and chlorine is passed in for 10 hours. The product is distilled (Gnehm, *A.* 238, 319).

Properties.—Plates (from water). V. sol. alcohol and ether, sl. sol. benzene and chloroform.

Reactions.—1. Converted by *heat* into H_2O and its anhydride.—2. Calcium salt gives octo-chloro-anthraquinone (in small quantity) when distilled (Kircher, *B.* 17, 1170).—3. *Sodium amalgam* reduces it in dilute alcoholic solution to phthalic acid (Claus a. Spruck, *B.* 15, 1401); the reduction is better performed in aqueous solution, but hydrophthalic acid and other products are also formed (Graebe, *A.* 238, 323).—4. HI and P at 230° give tetra-chloro-*s*-phenylene-dimethyl oxide, $C_6Cl_4<\genfrac{}{}{0pt}{}{CH_2}{CH_2}>O$, and some tetra-chloro-phthalide $C_6Cl_4<\genfrac{}{}{0pt}{}{CH_2}{CO}>O$. The latter body is also produced by the action of zinc-dust and glacial acetic acid.—5. PCl_5 forms $C_6Cl_4<\genfrac{}{}{0pt}{}{CCl_2}{CO}>O$ and $C_6Cl_4<\genfrac{}{}{0pt}{}{CCl_2}{CCl_2}>O$.

Salts.—K_2A''.—BaA 2⅓aq.—BaA'_2 3½aq (Tust, *B.* 21, 1532).—CuA'' 2aq. Ag_2A''.

Ethers.—Et_2A''. [60·5°].—$EtHA''$. [95°].—Me_2A''. [92°].

Anhydride $C_6Cl_4<\genfrac{}{}{0pt}{}{CO}{CO}>O$. [245°].

Chloride $C_6Cl_4<\genfrac{}{}{0pt}{}{CCl_2}{CO}>O$. [118°]. (336°) at 733 mm. From the anhydride and PCl_5 at 220°.

Tetrachloride $C_6Cl_4<\genfrac{}{}{0pt}{}{CCl_2}{CCl_2}>O$. [140°].

Imide $C_6Cl_4C_2O_2NH$. From NH_3 and the anhydride.

(γ)-CHLORO-ISO-PHTHALIC ACID $C_6H_3Cl(CO_2H)_2$. [278°]. S. ·026 at 15°.

Preparation.—A solution of amido-isophthalic acid in HCl is mixed at 0° with $NaNO_2$, and the pp. of the hydrochloride of diazo-isophthalic acid is gently warmed with HCl. Crystallised from water (Beyer, *J. pr.* 133, 506).

Properties.—Slender needles (from water). When dried over H_2SO_4 they contain water (½aq). V. sl. sol. hot water.

Salts. The neutral potassium salt gives no pp. with solutions of salts of Ca, Sr, Ba, Mg, Zn, Mn, Co, Ni, nor with $HgCl_2$. It gives, with $CdSO_4$, bulky white pp.; Fe_2Cl_6 light brown pp.; $Pb(OAc)_2$ and $AgNO_3$, white pps. soluble in hot water. $CuSO_4$, blue pp.; $Hg_2(NO_3)_2$, white gelatinous pp. $A''K_2$: needles arranged like ferns.—$A''Na_2$.—$A''Mg$ 7aq.—$A''Ca$ 2aq. S. 3 54 at 15°.—$A''Sr$ aq. S. ·929 at 15°.—$A''Ba$ 2aq. S. 1·41 at 15°.—$A''Cd$. S. ·303 at 15°.—$A''Ag_2$. Gelatinous pp. Crystallises in small needles (from hot water).

Ethyl ether $A''Et_2$ [45°]. Short prisms (from ether).

Chloro-tere-phthalic acid v. CHLORO-TEREPHTHALIC ACID.

DI-CHLORO-PHTHALIDE $C_6H_2Cl_2<\genfrac{}{}{0pt}{}{CH_2}{CO}>O$. [122°]. From the chloride of di-chloro-phthalic acid $C_6H_2Cl_2<\genfrac{}{}{0pt}{}{CCl_2}{CO}>O$ by reducing with Zn and HCl (Le Royer, *A.* 238, 355). Also from nitroso-di-chloro-phthalimidine and alkalis. Crystals (from alcohol).

- Di-chloro-phthalide $C_6H_2Cl_2<\genfrac{}{}{0pt}{}{CH_2}{CO}>O$ [1:4:5:6]. [163°]. Formed, together with di-chloro-(α)-naphthoquinone by oxidation of di-chloro-naphthalene [68°] with CrO_3 and glacial acetic acid. Short prisms or flat needles. Sol. alcohol and ether, v. sl. sol. water. Sublimable. It does not react with hydroxylamine (Guareschi, *B.* 19, 1155).

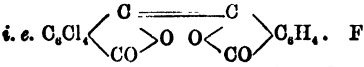
Tetra-chloro-phthalide $C_6Cl_4<\genfrac{}{}{0pt}{}{CH_2}{CO}>O$. [208·5°]. From tetrachlorophthalic anhydride, glacial HOAc and zinc-dust (Graebe, *A.* 238, 330). V. sl. sol. cold alcohol; insol. Na_2CO_3Aq; sol. boiling NaOH and reppd. by acids unaltered.

CHLORO-PHTHALIMIDE v. *Imide of* CHLORO-PHTHALIC ACID.

DI-CHLORO-PHTHALIMIDINE $C_6H_2Cl_2<\genfrac{}{}{0pt}{}{CH_2}{CO}>NH$. [210°]. From di-chloro-phthalimide, tin, and HCl (Royer, *A.* 238, 356)

Crystals (from chloroform). Gives a nitroso-derivative.

TETRACHLORO-DIPHTHALYL $C_{16}H_4Cl_4O_4$ *i. e.*



$$C_6Cl_4{<}\begin{matrix}C & = & C\\ & >O\ \ O< & \\ CO & & CO\end{matrix}{>}C_6H_4$$

Formed by the condensation of tetra-chloro-phthalide and phthalic anhydride without the use of sodium acetate (Graebe a. Guye, *A.* 233, 245). Brownish yellow powder; insol. alcohol, glacial acetic acid and toluene; sol. chloroform, aniline and phenol.

CHLOROPHYLL—the peculiar substance to which the green colour of leaves and other parts of plants is due—was first examined by Pelletier and Caventou, who called it *chlorophyll*. From the chemist's point of view it is simply an organic colouring matter, like indigo or alizarin.

It is important to bear this in mind, since much confusion and misunderstanding have arisen from the term chlorophyll having been applied to distinct things. Some chemists understand by chlorophyll the sum of the coloured constituents of leaves insoluble in water, and it has accordingly been proposed to call that constituent the colour of which inclines more to blue, *Kyanophyll*, while that constituent or group of constituents which gives solutions of a yellow or greenish-yellow tint should be named *Xanthophyll*. In works on vegetable physiology the term chlorophyll is sometimes applied to the complex of substances contained in living green cells, which take part in the process of assimilation and of which the colouring matter constitutes a portion, and chemists, following this example in giving a name to the whole which should have been confined to one part, have been led to ascribe to chlorophyll properties which no mere chemical substance can possibly possess. In order to avoid confusion it should therefore be understood that in using the term chlorophyll we mean simply the substance or it may be mixture of substances—to which the pure green colour of ordinary healthy leaves and of other vegetable organs, such as unripe fruit, is due. The appearance in leaves of any colour other than green, such as red, yellow, or purple, would indicate the presence of some substance accompanying the chlorophyll and disguising its colour or even replacing it entirely.

Chlorophyll is invariably present in vegetable cells in which the process of assimilation, *i.e.* the formation of organic matter from CO_2 and H_2O with elimination of O, is going on. Parasitic and other plants, such as fungi, which obtain their nutriment ready-formed from other organisms or from decaying organic matter, and do not decompose CO_2 in the same way as the majority of plants, contain no chlorophyll Plants or shoots grown in the dark from seeds or tubers are also devoid of chlorophyll; they grow at the expense of the matter stored up in the seed or tuber, and when this is exhausted they die. The appearance of chlorophyll in etiolated plants on exposure to light indicates the commencement of assimilation. It is certain, therefore, that chlorophyll plays some part in the process of assimilation, and that its presence is essential, but how it acts in assisting the process is unknown, its physical and chemical properties, so far as they are known to us, affording no certain clue to the solution of the problem. In the green cells of plants the chlorophyll is found associated with the protoplasmic constituent from which it may be easily separated by treatment with alcohol or ether. The green corpuscles seen in vegetable cells are in fact masses of albuminoid and other matters, permeated and tinged by chlorophyll, which is probably contained in a state of solution in the cell and not as a solid.

Physical and chemical properties of chlorophyll.—Considering the great importance of chlorophyll in relation to the process of assimilation in plants, it can hardly be a matter for surprise that it should very frequently have been examined. The literature of chlorophyll is very extensive, and comprises memoirs by physicists, chemists, and physiologists, some of them men of great eminence in their respective branches of science. Nevertheless, our knowledge of its properties, physical and chemical, is very scanty. The imperfect state of our knowledge of the subject is due to several causes. In the first place the quantity of chlorophyll contained in an extract of leaves, though the latter may be intensely coloured, is extremely small; secondly, chlorophyll is associated in the plant with large quantities of other substances, colouring matters, resins, fats, &c., which accompany it on extraction with ordinary solvents, and from which it cannot easily be separated; thirdly, it is a substance which is very apt to undergo change, so that during any process of purification to which it may be submitted, it will almost certainly be more or less altered; fourthly, chlorophyll, like most substances which play an important part in the vegetable or animal economy, is certainly amorphous, and the freedom from impurity of any specimen must therefore always be more or less doubtful. Some observers have described bodies which they have held to be crystallised chlorophyll, but the writer is of opinion that these were in all cases products of decomposition derived from chlorophyll. Chlorophyll contains nitrogen in addition to carbon, hydrogen and oxygen, but the percentage is certainly not large. It has been supposed to contain iron like the hæmoglobin of blood; after incineration a minute quantity of ferric oxide is indeed always found in the ash, but whether this is derived from chlorophyll, or from some substance or substances accompanying it, is uncertain. The ash also contains calcium and magnesium phosphates, but of these again it cannot with certainty be said that they are constituents of chlorophyll itself. Chlorophyll may be described as a neutral body, like indigo, having the properties neither of an acid nor a base; in constitution it may resemble the fats or the lecithins, as suggested by Hoppe-Seyler. Though not itself a glucoside, it is always found associated with a body having the characteristics peculiar to that class, as was first pointed out by the writer.

Chlorophyll is insoluble in water, but soluble in alcohol, ether, carbon disulphide and ethereal oils.

These solutions show a lively green colour of great intensity, accompanied by a marked red fluorescence. The solutions show an absorption spectrum which is quite characteristic, and must therefore be shortly described. A solution of chlorophyll made by extracting fresh green leaves with alcohol or ether is found, when very dark, to absorb nearly the whole spectrum, only a narrow strip of light at the extreme red end being visible. When the solution is made paler by the addition of more solvent, the green of the spectrum begins to appear, a faint absorption band showing itself about the middle. On still further diluting, other bands make their appearance in succession. When an average depth of colour is reached the following absorption bands are seen:—A very dark band beginning close to the line B and extending over C, followed by a second band between C and D which is much lighter, after which comes a third still paler one beyond D and close to the latter, lastly, a fourth band is seen partly on E which is usually the faintest of all, but is sometimes as dark as, and even darker than the third (see Fig. i.). Total obscuration begins about the line F. The four bands just described are usually marked with the numerals I.–IV. in accordance with the notation employed by Ångstrom, and are seen so constantly and invariably, when proper precautions are taken to have a solution of unchanged chlorophyll of average strength, as to constitute a certain test for chlorophyll, which may accordingly be defined as the substance which in solution shows this particular absorption spectrum. It should be mentioned that there is a considerable amount of obscuration throughout the whole spectrum of chlorophyll solutions, excepting only at the extreme red, so that the parts usually represented as white are in reality more or less darkened, and also that the bands, with the exception of band I., are not so sharply defined as the ordinary representations would lead one to suppose in consequence of the edges gradually shading off. Opinions differ as to whether the same absorption spectrum is seen when a green leaf is placed before the slit of a spectroscope, some observers maintaining that only band I. is discernible, while others say that all four bands can be made out, the only difference being that the bands are all shifted towards the red end, from which it has been inferred that in the plant chlorophyll exists in a state of solution, the solvent having a density greater than that of alcohol or ether. Returning to the solution of chlorophyll showing the spectrum just described, let us now see what takes place on further dilution. A beam of sunlight having been thrown on the slit of the spectroscope the solution is to be considerably diluted until it becomes quite pale. It will then be found that band I. having become narrower and paler has left the line C altogether and taken its place near B; band II. has become much narrower and paler but remained in the same place, while bands III. and IV. have entirely disappeared. At the other end of the spectrum, however, two pale, ill-defined bands have made their appearance, one being situated between F and G, the other on G (see Fig. ii.). These bands are numbered V. and VI. Whether they belong to chlorophyll itself or to some other colouring matter accompanying it is uncertain, no one having as yet succeeded in obtaining a solution of chlorophyll in which they are not seen, provided the solution is sufficiently dilute and is observed in sun-light. The writer is of opinion that the two bands belong to a yellow colouring matter (xanthophyll?) always accompanying chlorophyll, from which the latter cannot be separated. It is certain that all leaves contain a colouring matter, the chrysophyll of Hartsen (Bougarel's erythrophyll), which may be obtained in lustrous, orange-coloured crystals, and gives yellow solutions, showing two distinct absorption bands at the blue end not exactly in the same position as those just referred to—but no trace of any band in the other parts of the spectrum; the bands V. and VI. may belong to a nearly allied substance.

The absorption bands of chlorophyll solutions were first described by Sir D. Brewster, who was also the first to observe the red fluorescence of these solutions. The bands were next examined by Stokes and Ångström, by the latter of whom they were also correctly figured. Many other observers have worked on the same field; among these the following may be named: Askenasy, Gerland and Rawenhoff, Hagenbach, Harting, Kraus, L. Liebermann, Lommel, A. Meyer, Micheli, Morot, Pringsheim, Russell and Lapraik, Sacchse, Simmler, Sorby and Wiesner. The memoirs of Hagenbach, Kraus, Lommel, Pringsheim, Russell and Sorby on the subject are especially worthy of study. It should be mentioned that some of the absorption spectra figured in memoirs on chlorophyll really belong to derivatives of the latter. Whenever in such figures band IV. appears rather dark and is followed by another dark band nearer the blue end, we may conclude that the observer has worked with a specimen of chlorophyll that has undergone some change.

Products of decomposition of chlorophyll.—A solution of chlorophyll inclosed in a sealed tube and kept in the dark retains its colour for any length of time, but in an open vessel, especially when exposed to light, the colour disappears rapidly, only a faint yellow tinge remaining; what is formed during this change, which is doubtless due to oxidation, is not known.

By the action of acids chlorophyll undergoes a marked change, which no one who has worked with the substance can have failed to observe. When to an alcoholic solution of chlorophyll a small quantity of sulphuric or hydrochloric acid is added, the colour of the solution changes at once from a bright green to a dull yellowish-green or olive. Examined in the usual manner the spectrum will be found entirely altered; bands I. and II. have become more distinct from the clearing up of the space between the two, band III. appears much paler, and band IV. much darker, than before. After the solution has stood for some time band IV. will be found to have greatly increased in intensity, while another dark band has made its appearance near the line F just in front of the part where total obscuration begins. This is what has, not very appropriately, been called the absorption spectrum of *acid chlorophyll*, and is due to the formation of products derived from chlorophyll by a process the nature of which is not understood. That this process is not such a one as might admit of explanation by supposing chlorophyll to have the constitution of a salt, its acid constituent being expelled by the addition of a stronger acid, is proved by the fact that if alcoholic potash or soda be added in excess to a solution of chlorophyll which has been acted on by acids, the original bright green colour is not restored. To those conversant with the decomposition of complex organic substances, another explanation may suggest itself, viz. that the change is due to hydrolysis in presence of an acid, accompanied perhaps by a splitting up of the same kind as that which glucosides undergo when acted on by acids or ferments. Russell and Lapraik are of opinion that the change is a molecular, not a chemical one. Weak acids produce the same change as strong ones, but only after some time. On the addition of a comparatively large quantity of acetic acid to an alcoholic solution of chlorophyll, no change of colour is perceived at first, nor is the spectrum in any way altered, but on standing the colour slowly passes over to yellowish-green, and the same bands make their appearance as when a strong acid is employed. The same change frequently takes place when a solution of chlorophyll is left to stand in a loosely-stoppered bottle kept in the dark; in this case the effect is probably due to the presence of some substance, an ethereal oil for instance, which by oxidation yields an acid of some kind. Some leaves, such as those of the vine and virginian creeper, naturally contain much free acid which, on extraction of the leaves with alcohol, accompanies the chlorophyll and changes it after a short time.

In order to obtain the products derived from chlorophyll by the action of acids, fresh green leaves are extracted with boiling spirits of wine; the liquor after straining is allowed to stand, so that a portion of the fatty matter contained in it may be deposited, after which it is filtered and a current of hydrochloric acid gas is passed through it. By the action of the acid a dark brownish-green flocculent precipitate is formed, which after standing is filtered off and washed with alcohol. This precipitate contains two peculiar colouring matters, which Fremy named *phyllocyanin* and *phylloxanthin*, along with impurities of a fatty nature. The two colouring matters are separated by Fremy's method; the mixture is dissolved in ether, and the solution is shaken up with about a quarter its volume of concentrated ClH, whereupon it separates into two layers, an upper yellowish-green one containing phylloxanthin, and a lower bright-blue one containing phyllocyanin.

The phylloxanthin of the upper stratum is largely contaminated by fatty matter, from which it cannot easily be separated, but the phyllocyanin from the lower stratum can be purified and is obtained in microscopic crystals, which are generally opaque, but when very thin appear olive-coloured by transmitted light. The general properties of phyllocyanin have been described by the writer, but a few only of these can here be mentioned. Phyllocyanin is a body entirely *sui generis*, resembling no other natural colouring matter. It is insoluble in water and ligroin, but soluble in alcohol, ether, acetic acid, chloroform, benzene, and carbon disulphide. The solutions show an absorption spectrum with five bands (see Fig. iii.). It dissolves in concentrated ClH and SH_2O_4 giving solutions of a bright blue colour, and is reprecipitated unchanged by water. It dissolves in alkaline lyes, but is entirely changed by the action of the alkali. Its most interesting property is that of yielding by the combined action of acids, chiefly organic acids, and metallic oxides, such as cupric, ferrous and zinc oxides, compounds, the solutions of which are bright green and closely resemble solutions of chlorophyll not only in colour but in other respects also.

Phyllocyanin is remarkable for its great stability; its solutions remain for a long time unchanged when exposed to light and air, whereas solutions of chlorophyll are rapidly bleached under the same circumstances. Phyllocyanin yields with alkalis and reducing agents products which show absorption spectra of great variety and beauty (see Figs. v. and vi.). Phylloxanthin resembles phyllocyanin in many of its properties, but is a less interesting substance. Its absorption spectrum shows only four bands (see Fig. iv.). It will be seen that when the two substances are present together in solution, the bands of phylloxanthin will be concealed by those of phyllocyanin.

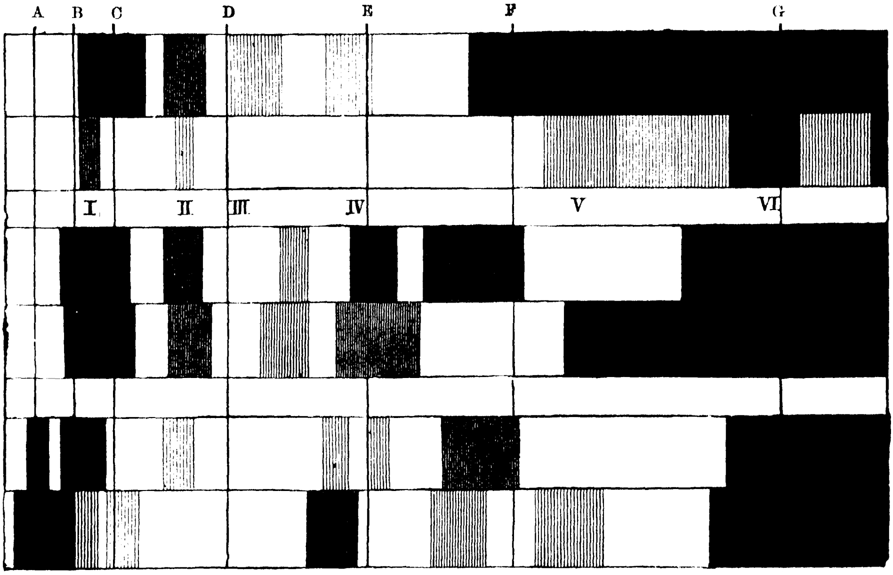
On reading some of the older memoirs on chlorophyll, such as those of Berzelius, Mulder, and Fremy, it will be evident that the authors worked not with chlorophyll itself, but with products due to the action of acids on the latter. It is probable that the *chlorophyllan* of Hoppe-Seyler and the *hypochlorin* of Pringsheim are products belonging to the same class as phyllocyanin and phylloxanthin. According to Tschirch chlorophyllan is the first product of the action of acids on chlorophyll, and splits up into phyllocyanin and phylloxanthin when the action of acid is prolonged. This short account may serve to show that our knowledge of the derivatives of chlorophyll is still very defective.

Chlorophyll in relation to plant life.—There can be no doubt that the presence of chlorophyll is necessary during the process of assimilation by plants, but what part it plays in the process is unknown. It was at first supposed, considering how powerfully the more refrangible end of the spectrum is absorbed by solutions of chlorophyll, that it was especially the blue rays that effected the decomposition of CO_2 and H_2O within the cells. This idea was soon abandoned in favour of another theory, according to which it is the red rays that are more active than the others in promoting assimilation, they being also strongly absorbed by chlorophyll. The latest investigations make it probable that the yellow rays, which are the least absorbed of any, produce a more abundant evolution of O, and consequently a greater amount of decomposition of CO_2 and H_2O than either the red or blue rays. Pringsheim is of opinion that chlorophyll acts simply as a screen which absorbing the less refrangible rays, moderates the energetic heating and oxidising action of the latter during the process of assimilation. All that can be positively asserted with regard to this part of the subject is that the colour, *i.e.* the absorptive power of chlorophyll has something to do with its mode of action.

It has been thought, and we often find it stated in books, that chlorophyll has itself the power of absorbing CO_2 and evolving O; attempts have even been made to prove that this takes place in ordinary solutions of chlorophyll. This is, however, erroneous; it is certain that the complex which physiologists call the chlorophyll corpuscle, or simply chlorophyll, has the power of decomposing CO_2 and H_2O with evolution of O, but that any such power resides in the colouring matter when dissociated from the other constituents of the complex must be incorrect, since it is opposed to all that we know of the chemical properties of organic substances.

List of the most important memoirs and works on chlorophyll:—

Ångström, *Ueb. d. grüne Farbe d. Pflanzen*, *P.* 93, 475; Askenasy, *Bot. Ztg.*, 1867, 225; **Berzelius**, *Untersuchung d. Blattgrüns*, *A.* 27, 296; Brewster, *On the Colours of Natural Bodies*, *T. E.* 12, 588; Chautard, *Examen spectroscopique de la chlorophylle*, *C. R.* 76, 103, 570, 1031, 1066, 1273; Filhol, *C. R.* 61, 371; 66, 1218; 79, 612; Fremy, *Sur la matière colorante verte des feuilles*, *C. R.* 50, 405; 61, 188; Gautier, *Sur la chlorophylle*, *C. R.* 89, 862; Gerland and Rawenhoff, *Recherches sur la chlorophylle*, *Ar. N.* 6, 97; Hagenbach, *Untersuchungen üb. d. optischen Eigenschaften d. Blattgrüns*, *P.* 141, 245; Harting, *P.* 96, 543; Hansen, '*Der Chlorophyllfarbstoff*,' *Arb. d. bot. Inst. in Würzburg*, 3, 1; Hartsen, *C. C.* 1872, 524, 1875, 618; Hoppe-Seyler, *Ueber d. Chlorophyll d. Pflanzen*, *H.* 3, 1879, 339; 4, 1880, 193, 5, 1881, 75; **Kraus**, *Zur Kenntniss d. Chlorophyllfarbstoffe*, Stuttgart, 1872; Kromeyer, *Zerlegung des Chlorophylls in einem blauen und einem gelben Farbstoff*, *Ar. Ph.* 155, 164; L. Liebermann, *Sitz. W.* 72, 599; Lommel, *Ueb. d. Verhalten d. Chlorophylls zum Licht*, *P.* 143, 568; Meyer, *Das Chlorophyllkorn*, Leipzig, 1883; Micheli, *Arch. d. Sc. de la bibl. univ. d. Genève*, Mai 1867; Morot, *Ann. des Sc. Nat.* 3rd ser. 13, 160; Mulder, *Ueber d. Chlorophyll*, *J. pr.* 33, 478; Pelletier et Caventou, *Sur la matière verte des feuilles*, *A. Ch.* 9, 194; Pfaundler, *A.* 115, 37; Pringsheim, *Untersuchungen üb. Lichtwirkung u. Chlorophyllfunction in d. Pflanzen*, Leipzig, 1881; Russell and Lapraik, *A Spectroscopic Study of Chlorophyll*, *C. J.* 41, 334; Sachsse, *Die Chem. u. Physiol d. Farbstoffe*, Leipzig, 1877; Schunck, *Contributions to the Chemistry of Chlorophyll*, *Pr.* 39, 348, 42, 184; Simmler, *P.* 115, 603; Sorby, *Comparative Vegetable Chromatology*, *Pr.* 21, 452; Stokes, *On the supposed identity of Biliverdin with Chlorophyll, with remarks on the Constitution of Chlorophyll*, *Pr.* 13, 144; Tschirch, *Untersuchungen üb. d. Chlorophyll*, Berlin, 1884; Verdeil, *Recherches s. la mat. col. verte des feuilles*, *C. R.* 33, 689; *Wiesner*, *Bemerkungen üb. d. angebl. Bestandtheile d. Chlorophylls*, Flora, 1874, 278. E. S.



Explanation of Cut.

Fig. i.—Absorption spectrum of chlorophyll, strong solution.
„ ii. „ „ „ „ weak „
„ iii. „ „ „ phyllocyanin.
„ iv. „ „ „ phylloxanthin.
„ v. „ „ „ a phyllocyanin derivative.
„ vi. „ „ „ ethyl compound of the preceding.

CHLORO-PICOLINE *v.* Chloro-methyl-pyridine.

CHLORO-PICOLINIC ACID *v.* Chloro-pyridine carboxylic acid.

CHLOROPICRIN *v.* Tri-chloro-nitro-methane.

CHLOROPLATINATES *v.* platinates under Platinum.

CHLORO-PROPANE *v.* Propyl Chloride.

ωα-Di-chloro-propane $C_3H_6Cl_2$ *i.e.* $CH_3.CHCl.CH_2Cl$. *Propylene chloride.* Mol. w. 113. (97° cor.). S.G. ^{0} 1·584; ^{14} 1·155 (F. a. S.); ^{14} 1·166 (Linnemann, *A.* 161, 62).

Formation.—1. From chlorine and propylene (Cahours, *A.* 76, 283; Reynolds, *A.* 77, 124).—2. From chloro-iodo-propane and Cl (Friedel a. Silva, *C. R.* 76, 1596).—3. From propane and Cl (Schorlemmer, *Pr.* 17, 372; *A.* 150, 214).—4. Together with $CH_3.CCl_2.CH_3$, by chlorinating $CH_3.CHCl.CH_3$ in sunshine (Friedel a. Silva, *Bl.* [2] 16, 3).—5. From isopropyl chloride and ICl (Friedel a. Silva, *C. R.* 73, 1380).—6. From allyl chloride and conc. HCl at 100° (Reboul, *A. Ch.* [5] 14, 453).

Reactions.—1. Alcoholic KOH gives α-chloro-propylene $CH_3.CCl:CH_2$ (Friedel a. Silva, *A. Ch.* [4] 16, 349).—2. *Water* (20 vols.) at 220° gives propionic aldehyde and acetone. Water and PbO at 150° give propylene glycol (Eltekoff, *B.* 6, 558).—3. Conc. HI at 150° gives isopropyl chloride.

ωω-Di-chloro-propane $CH_3.CH_2.CHCl_2$. *Propylidene chloride.* (86°). S.G. ^{10} 1·143. Formed, together with chloro-propylene $CH_3.CH:CHCl$, by the action of PCl_5 on propionic aldehyde (Reboul, *A. Ch.* [5] 14, 458). Alcoholic KOH gives $CH_3.CH:CHCl$ (34°).

αα-Di-chloro-propane $CH_3.CCl_2.CH_3$. *Chloracetol. Methylchloracetol.* (70°). S.G. $\frac{15}{15}$ 1·0966; $\frac{25}{25}$ 1·0848 (Perkin, *C. J.* 45, 529); ^{10} 1·827 (Linnemann, *A.* 161, 67). H.F.p. 42080. H.F.v. 40340 (*Th.*).

Formation.—1. From acetone and PCl_5 (Friedel, *A.* 112, 236).—2. From isopropyl chloride and Cl (Friedel a. Silva, *Z.* 1871, 489). 3. From allylene and fuming HCl in the cold (Reboul, *A. Ch.* [5] 14, 453).

Reactions.—1. Alcoholic KOH forms α-chloro-propylene $CH_3.CCl:CH_2$ (24°). 2. AgOBz gives $(CH_3)_2C(OBz)_2$. 3. *Water* (8 vols.) at 170° gives acetone (Oppenheim, *B.* 2, 213).

ωβ-Di-chloro-propane $CH_2Cl.CH_2.CH_2Cl$. *Trimethylene chloride.* (119°). S.G. ^{15} 1·201 (R.); $\frac{17·6}{4}$ 1·1896 (F.). From the corresponding dibromide and $HgCl_2$ at 180° (Reboul, *A. Ch.* [5] 14, 453). Formed also from trimethylene glycol $CH_2OH.CH_2.CH_2OH$ and HCl (Freund, *M.* 2, 638). Alcoholic KOH gives allyl chloride.

ωαβ-Tri-chloro-propane $C_3H_5Cl_3$ *i.e.* $CH_2Cl.CHCl.CH_2Cl$. *Trichlorhydrin. Glyceryl chloride. Allyl trichloride.* (158°). S.G. $\frac{15}{15}$ 1·3984; $\frac{25}{25}$ 1·3878 (Perkin, *C. J.* 45, 532); ^{0} 1·41 (O.). M.M. 7·897 at 21·6°.

Formation.—1. From glycerin dichlorhydrin (di-chloro-propyl alcohol) and PCl_5 (Berthelot a. De Luca, *A. Ch.* [3] 48, 304; 52, 433; Fittig, *A.* 135, 359).—2. By passing Cl into allyl iodide under water (Oppenheim, *Bl.* [2] 2, 97).—3. One of the products of chlorination of propylene chloride (Belohoubek, *B.* 9, 924), or of propane (?) (Berthelot, *A.* 155, 105). 4. From propylene chloride and ICl at 160° (Friedel a. Silva, *Z.* 1871, 683).

Reactions.—1. *Water* (20 vols.) by heating at 160° for 24 hours forms glycerin.—2. KOH gives $CH_2:CCl.CH_2Cl$ (101°) and a little $CHCl:CH.CH_2Cl$.—3. Alcoholic KSH gives $C_3H_5(SH)_3$.—4. Alcoholic NH_3 forms $(C_3H_4Cl)_2NH$.—5. Al_2I_6 gives allyl iodide (Gustavson, *C. C.* 1877, 19).

ωωω-Tri-chloro-propane $CH_3.CH_2.CCl_3$ (145°–150°). From Pr_2S and dry Cl in daylight (Spring a. Lecrenier, *Bl.* [2] 48, 623). Ag_2O converts it into propionic acid.

ωωα-Tri-chloro-propane $CH_3.CHCl.CHCl_2$. *α-Chloro-propylidene chloride.* (140°). S.G. $\frac{0}{4}$ 1·402; ^{25} 1·372. Formed by chlorination of propylene or propylidene chloride in sunshine. Also, together with the preceding, by heating propylene chloride with ICl at 160° (Friedel a. Silva, *C. R.* 74, 805). Formed by union of $CH_3.CCl:CH_2$ with Cl (Berthelot, *A.* 155, 105).

ωαα-Tri-chloro-propane $CH_3.CCl_2.CH_2Cl$ (123°). S.G. ^{0} 1·350; ^{25} 1·318.

Formation.—1. From $CH_3.CCl_2.CH_3$ by Cl in sunshine, or by ICl (F. a. S.).—2. From propylene chloride and Cl (Belohoubek, *B.* 9, 924). 3. From chloro-acetone and PCl_5.—4. From $CH_3.CCl:CH_2$ and Cl at 0° in sunshine.

Reactions.—1. *Water* at high temperatures forms $CH_3.CO.CHO$ (?).—2. Alcoholic KOH gives two di-chloro-propylenes (75°) and (94°) (Friedel a. Silva, *C. R.* 74, 806).

Tri-chloro-propane $CH_2Cl.CH_2.CHCl_2$. *β-Chloro-propylidene chloride.* (147°). S.G. ^{14} 1·362. V.D. 4·95. Formed by the action of PCl_5 on β-chloro-propionic aldehyde or on acrolein (Geuther, *Z.* 1865, 29; van Romburgh, *Bl.* [2] 37, 98). Alcoholic KOH gives di-chloro-propylene $CH_2:CH.CHCl_2$.

Tetra-chloro-propane $CH_3.CCl_2.CHCl_2$. (153°). S.G. ^{13} 1·47. From di-chloro-acetone and PCl_5 (Borsche a. Fittig, *A.* 133, 114). Also from allylene dichloride (Pinner, *A.* 179, 47). Apparently the same body is formed as a by-product in the preparation of tri-chloro-butyric aldehyde by chlorinating aldehyde (Pinner, *B.* 10, 1057). Alcoholic KOH gives $C_3H_3Cl_3$ (115°).

Tetra-chloro-propane $C_3H_4Cl_4$ *i.e.* $CH_2Cl.CH_2.CH_3$? [178°]. (203°). From propane and Cl in sunshine (Schorlemmer, *Pr.* 18, 29). Stellate groups of needles (from alcohol). Smells like camphor.

Tetra-chloro-propane $CH_2Cl.CCl_2.CH_2Cl$. *Iso-allylene tetrachloride.* (164°). S.G. ^{17} 1·496. From $CH_2Cl.CCl:CH_2$ (95°) and Cl or HOCl (Fittig a. Pfeffer, *A.* 135, 360; Henry, *C. R.* 94, 1428). Also from $CH_3.CCl:CH_2$ and Cl (Berthelot, *A.* 155, 105). Alcoholic KOH gives C_3H_5Cl. Alcoholic NH_3 gives $(C_3H_3Cl_2)_2NH$. Sodium gives allylene.

Tetra-chloro-propane $C_3H_4Cl_4$ *i.e.* $CH_3.CHCl.CCl_3$. [145°]. (c. 185°). From isopropyl iodide and Cl. Resembles camphor (B.).

Tetra-chloro-propane $C_3H_4Cl_4$. (c. 198°). S.G. 1·55. From propylene chloride and Cl (Cahours, *A.* 76, 283). Probably identical with the preceding or, possibly, with the following.

Tetra-chloro-propane $CH_2Cl.CHCl.CHCl_2$. *Tetra-chloro-glycide. Allylidene tetrachloride.* (180°). S.G. $\frac{15}{4}$ 1·521. V.D. 6·3. From $CH_3.CCl:CH_2Cl$ and Cl (Hartenstein, *J. pr.* [2] 7, 313). From $CH_2:CH.CHCl_2$ and Cl (van Romburgh, *Bl.* [2] 36, 553).

Penta-chloro-propane $C_3H_3Cl_5$ *i.e.* $CH_2Cl.CCl_2.CHCl_2$. (194°). From di-chloro-acetone and PCl_5 (Borsche a. Fittig, *A.* 133, 116). Alcoholic KOH gives $C_3H_2Cl_4$ (165°).

Penta-chloro-propane $C_3H_3Cl_5$ *i.e.* $CH_3.CCl_2.CCl_3$? From $CH_3.CCl_2.CHCl_2$ and Cl (B. a. F.). Prisms.

Penta-chloro-propane $C_3H_3Cl_5$. (c. 223°). From propylene chloride and Cl (Cahours, *A.* 76, 283).

Hexa-chloro-propane $C_3H_2Cl_6$ *i.e.* $CCl_3.CH_2.CCl_3$? (250°). Formed by chlorinating propane in the brightest sunshine (Schorlemmer, *Pr.* 18, 29). Liquid, smelling like camphor.

Hexa-chloro-propane $C_3H_2Cl_6$ *i.e.* $CCl_3.CHCl.CHCl_2$? (c. 243°). S.G. 1·63. From propylene chloride and Cl (Cahours, *A.* 76, 283).

Hepta-chloro-propane C_3HCl_7. (260°). S.G. 1·73. From propylene chloride and Cl (Cahours).

Per-chloro-propane C_3Cl_8. [160°]. (269°). From $CH_2Cl.CHCl.CH_2Cl$ and ICl_3 at 200°. Formed also, together with CCl_4, by heating isobutane with ICl_3 at 240° (Krafft a. Merz, *B.* 8, 1045); and, together with C_2Cl_6 and CCl_4 by the action of ICl_3 on isobutyric acid (Krafft, *B.* 9, 1085). Crystalline mass; v. e. sol. alcohol, ether and ligroin. At 250° it splits up into C_2Cl_4 and CCl_4.

CHLORO-PROPANE SULPHONIC ACID $C_3H_6Cl.SO_3H$. From the product of the action of ICl_3 on propane sulphonic acid at 160° the salts $(C_3H_6ClSO_3)_2Ba(C_3H_7SO_3)_2Ba$ aq and $(C_3H_6ClSO_3)_2Ba3(C_3H_7SO_3)_2Ba$ may be isolated (Spring a. Winssinger, *B.* 16, 328).

α-CHLORO-PROPIONIC ACID $C_3H_5ClO_2$ *i.e* $CH_3.CHCl.CO_2H$. Mol. w. 108½. (186°). S.G. ^{0} 1·28.

Preparation.—Calcic lactate (17 g.) is shaken with PCl_5 (40 g.) and distilled from a bath of H_2SO_4. The distillate is mixed in the cold with the requisite quantity of cold water. The yield is 60 per cent. (J. M. Lovén, *J. pr.* [2] 29, 366; *cf.* Wurtz, *A.* 107, 192; Ulrich, *A.* 109, 271; Lippmann, *A.* 129, 81; Buchanan, *Z.* [2] 4, 523; Brühl, *B.* 9, 35; Mazzara, *G.* 12, 261).

Properties.—Liquid, miscible with water; blisters the skin.

Reactions.—1. *Zinc* and HCl convert it into propionic acid.—2. The solutions of the Ba and Ag salts change to lactate on boiling.—3. With conc. solution of KHS (2 mols.) it gives thiolactate and thiodilactylate of potassium.

Salts.—AgA′.—BaA′$_2$.

Methyl ether MeA′. (182½°). S.G. ^{4} 1·075. μ_D 1·423 (Kahlbaum, *B.* 12, 344).

Ethyl ether EtA′. (147°). S.G. $\frac{20}{4}$ 1·0869. μ_β 1·4237. R_∞ 51·12 (Brühl, *A.* 203, 24). *Reactions.*—1. When heated with *thiurea* 5 hours at 100° it gives the hydrochloride of lactylthio-urea: $CS<\begin{matrix}NH.C_2H_4\\NH.CO\end{matrix}$.—2. With *potassic sulphocyanide* 5 hours at 150° it gives $CH_3.CH(SCN).CO_2Et$ (Freytag, *J. pr.* 128, 380). 3. NaOEt gives $CH_3.CH(OEt).CO_2Et$.

Amide $CH_3.CHCl.CONH_2$. [80°]. Scales; v. sol. water (Beckurts a. Otto, *B.* 9, 1592).

Chloride $CH_3.CHCl.COCl$. (110°). V.D. 4·38. S.G. $^{7\cdot5}$ 1·239 (Henry, *C. R.* 100, 114).

Nitrile $CH_3.CHCl.CN$. (122°). Pungent liquid.

β-Chloro-propionic acid $CH_2Cl.CH_2CO_2H$. [41°]. (B. a. O.); [38°] (H.). (204°).

Formation.—1. By heating hydracrylic acid with fuming HCl at 120° (Beckurts a. Otto, *B.* 18, 226).—2. From its chloride, which is formed by the union of ethylene with $COCl_2$ (Lippmann, *A.* 129, 81; Henry, *C. R.* 100, 114).—3. From acrylic acid and HCl (Linnemann, *A.* 163, 95).—4. From β-iodo-propionic acid and chlorine-water (Richter, *Z.* 1868, 451).

Properties.—White plates; v. e. sol. water and alcohol. Does not blister the skin.

Methyl ether MeA′. (156°).

Ethyl ether EtA′. (163°). V.D. 4·94. S.G. ^{8} 1·116.

Chloro-ethyl ether $CH_2Cl.CH_2A'$. (c. 213°). S.G. ^{8} 1·282. From the acid and $CH_2OH.CH_2Cl$ (H.).

Chloride $CH_2Cl.CH_2.COCl$. (144°). V.D. 4·42. S.G. ^{13} 1·331.

αα-Di-chloro-propionic acid $CH_3.CCl_2.CO_2H$. (c. 188°).

Formation.—1. From pyruvic acid and PCl_5 (Klimenko, *B.* 3, 465; 5, 477; Beckurts a. Otto, *B.* 11, 386).—2. The nitrile is formed by chlorinating propionitrile (Otto, *A.* 132, 181; *B.* 9, 1877).

Properties.—Liquid; v. sol. water; insol. conc. HCl. Solidified by cold. Converted by zinc and HCl into propionic acid. Water at 140° gives pyruvic acid. Boiling alcoholic KOH gives α-chloro-acrylic acid. Reduced silver forms $CO_2H.CMe{:}CMe.CO_2H$ and $CO_2H;CMeCl.CMeCl.CO_2H$.

Salts. — NH_4A'. — KA′ 6aq. — BaA′$_2$ aq. — CaA′$_2$ aq.—CaA′$_2$ 3aq.—ZnA′$_2$ aq: easily soluble flat needles.—AgA′.—On heating with water it decomposes into pyruvic acid, dichloropropionic acid, and AgCl. On heating the dry salt it yields pyruvic-dichloropropionic anhydride $\begin{matrix}CH_3.CO.CO\\CH_3.CCl_2.CO\end{matrix}>O$ and AgCl (Beckurts a. Otto, *B.* 18, 227).

Methyl ether MeA′. (144°).

Ethyl ether EtA′. (157°) (B. a. O.); (160°) (K.). S.G. ^{0} 1·249.

Isobutyl ether CH_2PrA'. (184°).

Allyl ether C_3H_5A'. (177°).

Chloride $CH_3.CCl_2.COCl$ (c. 110°).

Anhydride $(CH_3.CCl_2.CO)_2O$. (191°).

Amide $CH_3.CCl_2.CONH_2$. [116°]. Monoclinic laminæ (Haushofer, *Z. K.* 7, 267).—$(CH_3.CCl_2.CONH)_2Hg$ aq: needles.

Nitrile $CH_3.CCl_2.CN$. (105°). S.G. ^{15} 1·431.

Paranitrile $(CH_3CCl_2)_3C_3N_3$(?). [74°]. S. (alcohol) 14 at 20°. Chlorine acting upon propionitrile forms a liquid di-chloro-propionitrile (104°-107°) and a solid isomeride [74°]; the formation of the latter is promoted by a low temperature. Both give the same di-chloro-propionic acid on saponification, hence the solid form is probably a polymeride of the liquid. The liquid form sometimes changes spontaneously into the solid form (Otto a. Voigt, *J. pr.* [2] 36, 79). *Reactions of the paranitrile.*—1. H_2SO_4 (1 vol.) mixed with water (1 vol.) at 180° gives α-di-chloropropionic acid.—2. Alcoholic NH_3 gives di-chloro-propionamide. — 3. *Zinc and acetic acid* reduce it to $(C_2H_5)_3C_3N_3$ (195°).—4. *Zinc* acting on a solution in dilute alcohol forms a base $C_9H_{16}N_2$, [111°], (c. 273°), crystallising from petroleum ether in needles or plates, v. sol. ether and alcohol, v. sl. sol. water. It forms salts: B′HCl.—$B'_2H_2PtCl_6$.—$AgC_9H_{15}N_2$ ½aq.

αβ-Di-chloro-propionic acid $CH_2Cl.CHCl.CO_2H$. [50°]. (210°).

Formation.—1. From glyceric acid and HCl (Werigo, *B.* 12, 178; *cf.* *A.* 170, 163).—2. From di-chloro-propyl alcohol $CH_2Cl.CHCl.CH_2OH$ by oxidation (Henry, *B.* 7, 414; Werigo a. Melikoff, *B.* 10, 1500).—3. From α-chloro-acrylic acid and HCl at 180° (W. a. M.).—4. Formed from $CH_2(OH).CHCl.CO_2H$ and fuming HCl at 100° (Melikoff, *J. R.* 13, 163; *C. C.* 1881, 354).

Properties. Small needles. Alcoholic KOH gives α-chloro-acrylic acid.—HO.PbA'.

Ethyl ether EtA'. (184°). S.G. $\frac{20}{4}$ 1·2461. μ_β 1·4538. R_∞ 59·75 (Brühl, *A.* 203, 25). Successive treatment with alcoholic KCy and KOH gives fumaric and inactive malic acids (Werigo a. Tanatar, *A.* 174, 367).

ββ-Di-chloro-propionic acid $CHCl_2.CH_2.CO_2H$. [56°]. From β-chloro-acrylic acid and aqueous HCl at 80° (Otto a. Fromme, *A.* 239, 268). Prisms, v. sol. alcohol, ether, benzene, chloroform, and water. Converted by alcoholic KOH into $CHCl{:}CH.CO_2H$.

Ether EtA'. (171°-175°).

Amide $CHCl_2.CH_2.CO.NH_2$. [140°]: needles.

Tri-chloro-propionic acid (?) $C_3H_3Cl_3O_2$ (?). [60°]. From per-chloro-succinic ether and conc. KOHAq (Malaguti, *A. Ch.* [3] 16, 67, 72, 82).—AgA'.

β-CHLORO-PROPIONIC ALDEHYDE C_3H_5ClO *i.e.* $CH_2Cl.CH_2.CHO$. *Acroleïn hydrochloride.* (c. 45°) at 10 mm. (130°-170°). Formed, together with the paraldehyde, by passing gaseous HCl into acrolein (Geuther a. Cartmell, *A.* 112, 3; Krestownikoff, *J. R.* 11, 249; Grimaux a. Adam, *C. R.* 92, 300). Liquid. Reduces Fehling's solution. Rapidly changes to the solid paraldehyde. HNO_3 forms β-chloro-propionic acid.

β-Chloro-propionic paraldehyde $(C_3H_5ClO)_3$ (?). [33·5°]. (170°-175°) at 15 mm. Formed by spontaneous polymerisation of the preceding, into which it is reconverted by distillation under ordinary pressure. Needles. Insol. water. It does not reduce Fehling's solution. Not acted upon by water or baryta at 100°, nor by AgOAc or $Pb(OAc)_2$ at 120°. Water at 120° gives HCl and metacrolein. Distillation over solid KOH also forms some metacroleïn.

αβ-Di-chloro-propionic aldehyde $CH_2Cl.CHCl.CHO$. From acrolein and Cl (Aronstein, *A. Suppl.* 3, 190). Oil. Its alcoholate $CH_2Cl.CHCl.CH(OH)(OEt)$ boils at 150°-155°.

β-CHLORO-PROPYL ALCOHOL C_3H_7ClO *i.e.* $CH_2Cl.CH_2.CH_2OH$. *Trimethylene chlorhydrin.* (161° cor.). S.G. ^{17} 1·132. S. 50. From trimethylene glycol $CH_2OH.CH_2.CH_2OH$ and HCl at 100° (Reboul, *A. Ch.* [5] 14, 491).

α-Chloro-isopropyl alcohol $CH_3.CH(OH).CH_2Cl$. *Propylene chlorhydrin.* (128°). S.G. ^{0} 1·130.

Formation.—1. From propylene glycol and HCl (Oser, *A. Suppl.* 1, 254) or S_2Cl_2 (Morley, *B.* 18, 1805).—2. From allyl chloride (1 pt.) and conc. H_2SO_4 (3 pts.) at 100°; the product being distilled with water (10 pts.) (Oppenheim, *A. Suppl.* 6, 367).—3. From propylene and HOCl (Markownikoff, *Z.* 1870, 423).

Properties.—Liquid, sol. water. May probably contain $CH_3.CHCl.CH_2OH$.

Reactions.—1. P_2O_5 gives allyl chloride and chloro-propylene (Henry, *Z.* 1871, 600).—2. The chlorhydrin obtained by the action of S_2Cl_2 upon propylene glycol gives chloro-acetone on oxidation with $K_2Cr_2O_7$ and H_2SO_4, or with HNO_3 (Morley a. Green, *B.* 18, 24; *C. J.* 47, 132). The chlorhydrin obtained from propylene and HOCl is oxidised (by chromic mixture) to chloro-acetone according to Markownikoff, or (by HNO_3) to α-chloro-propionic acid according to Henry (*B.* 7, 1649, 1790).—3. HNO_3 gives chloro-acetic acid (Henry, *Bl.* [2] 25, 389).—4. Heating with ZnO or PbO gives propionic aldehyde and acetone (Eltekoff, *J. R.* 10, 222).

Benzoyl derivative C_3H_6ClOBz. (269° cor.). S.G. ^{10} 1·172; ^{45} 1·149. From the alcohol and BzCl. Oil. Alkalis form propylene oxide. $ZnEt_2$ gives propylene ethyl phenyl ketate $C_3H_6{<}^{O}_{O}{>}CEt.C_6H_5$ (Morley a. Green, *C. J.* 47, 134; *B.* 17, 3015).

Ethyl ether $CH_3.CH(OEt).CH_2Cl$. (118°). S.G. ^{0} ·984. From di-chloro-di-ethyl oxide and $ZnMe_2$ (Lieben, *A.* 146, 225; 178, 14).

αβ-Di-chloro-propyl alcohol $CH_2Cl.CHCl.CH_2OH$. *Dichloride of allyl alcohol.* (182°). S.G. ^{0} 1·380 (T.); $^{17.5}$ 1·355 (G.).

Formation.—1. From allyl alcohol and Cl (Tollens, *A.* 156, 164; Hübner a. Müller, *A.* 159, 168).—2. From allyl chloride and HOCl (v. Geyerfeldt, *A.* 154, 247; *B.* 6, 720; Henry, *B.* 3, 352; 7, 414).—3. Together with its isomeride, by passing dry HCl into glycerin (Fauconnier a. Sanson, *Bl.* [2] 48, 236). According to Markownikoff (*A.* 208, 349) passing HCl into a mixture of glycerin and aqueous HCl only produces $CH_2Cl.CH(OH).CH_2Cl$ (*cf.* Tollens, *Z.* 1869, 174).

Properties.—Viscid oil, sl. sol. water, sol. alcohol. Aqueous NaOH gives epichlorhydrin (119°). HNO_3 gives αβ-di-chloro-propionic acid.

Di-chloro-isopropyl alcohol $C_3H_6Cl_2O$ *i.e.* $CH_2Cl.CH(OH).CH_2Cl$. *Glycerin dichlorhydrin.* Mol. w. 129. (176° i.V.). S.G. ^{0} 1·383; ^{19} 1·367 (Markownikoff, *A.* 208, 349). S. 11 at 19°.

Formation.—1. From glycerin and HCl (Berthelot, *A.* 92, 302; Hübner a. C. Müller, *Z.* [2] 6, 344; Watt, *B.* 5, 257).—2. From glycerin and S_2Cl_2 (Carius, *A.* 122, 73; Claus, *A.* 168, 42).—3. From epichlorhydrin and fuming HCl (Reboul, *A. Suppl.* 1, 225).—4. Together with its isomeride, by the union of HOCl with allyl chloride (Henry, *B.* 3, 352).

Reactions.—1. *Chromic acid mixture* oxidises it to s-di-chloro-acetone [43°] and chloro-acetic acid.—2. *Sodium amalgam* converts it into isopropyl alcohol (Buff, *A. Suppl.* 5, 250).—3. *Sodium* added to its ethereal solution forms allyl alcohol (H. a. M.; Tornöe, *B.* 21, 1282).—4. Alcoholic (4 p.c.) NH_3 ($2\frac{1}{4}$ mols.) forms amorphous 'chlorhydrinimide' $C_{12}H_{27}N_3Cl_2O_4$. Weaker alcoholic NH_3 (1 p.c.) forms hydrochlorides of 'diamido-hydrin' $C_3H_{10}N_2O$, and of 'glycidamine' C_3H_7NO (Claus, *A.* 168, 29; *B.* 8, 244).—5. *Aniline* forms C_3H_6ONPh.—6. Solid NaOH gives epichlorhydrin C_3H_5ClO.—7. Br at 100° gives di-chloro-di-bromo-acetone $CBr_2Cl.CO.CH_2Cl$ and chloro-tri-bromo-acetone (Grimaux a. Adam, *Bl.* [2] 32, 18).—8. P_2O_5 acts vigorously, forming di-chloro-propylene.

Formyl derivative $CH_2Cl.CH(OCHO).CH_2Cl$. (c. 152°) at 22 mm. Formed by heating the alcohol with nitro-methane at 220° (Pfungst, *J. pr.* [2] 34, 28). The nitro-methane may perhaps first form hydroxylamine and formic acid: $CH_3NO_2 + H_2O = CH_2O_2 + NH_3O$; but no hydroxylamine could be found.

Acetyl derivative $CH_2Cl.CH(OAc).CH_2Cl$. (204°) (B. a. L.; T.); (195°) (H.); (c. 142° at 25 mm.) (P.). S.G. ^{11} 1·283 (T.); ^{8} 1·274 (H.).

Formation.—1. From glycerin and AcCl.—2. By passing HCl at 100° into a mixture of glycerin and HOAc (Berthelot a. De Luca, *A. Ch.* [3] 52, 459).—2. From $CH_2Cl.CH(OH).CH_2Cl$ and AcCl (Henry, *B.* 4, 704).—3. From epichlorhydrin and AcCl (Truchot, *A.* 138, 297).—4. From the formyl derivative and AgOAc (Pfungst, *J. pr.* [2] 34, 28).

Butyryl derivative $(CH_2Cl)_2CH.O.CO.C_3H_7$. (227°). S.G. ^{11} 1·194 (T.).

Isovaleryl derivative $(CH_2Cl)_2.CH.O.CO.C_4H_9$. (245°) at 737 mm. S.G. ^{11} 1·149 (Truchot, *A.* 138, 297).

Benzoyl derivative $(CH_2Cl)_2CH.OBz$. (222°) at 40 mm. S.G. ^{8} 1·441. From epichlorhydrin and BzCl at 180° (T.). Also from the formyl derivative and BzCl (P.).

Tri-chloro-isopropyl alcohol $CCl_3.CH(OH).CH_3$. [49°]. (150°–160°). From chloral by successive treatment with $ZnMe_2$ and water (Garzarolli-Thurnlackh, *A.* 210, 77). Small deliquescent needles (from ether). May be sublimed. Smells like camphor.

TRI-CHLORO-PROPYLAMINE $C_3H_4Cl_3.NH_2$. Formed by the action of Sn and HCl on dinitro-allylene-dichloride $C_3H_4Cl_2(NO_2)_2$ (Pinner, *A.* 179, 55). Oil; may be distilled.

β-CHLORO-α-PROPYL-CINNAMIC ACID $C_6H_5.CCl:C(C_3H_7).CO_2H$. [121°]. From its ether, which is formed by treating propyl-benzoyl-acetic ether with PCl_5 (W. H. Perkin, jun., *C. J.* 49, 163). Triclinic prisms; $a:b:c = ·797:1:·710$; $\alpha = 122°33'$; $\beta = 106°21'$; $\gamma = 69°25'$ (Haushofer). May be sublimed. V. sol. alcohol, ether, benzene, chloroform, and HOAc; m. sol. ligroin.

Ethyl ether EtA′. (248°) at 300 mm. Oil.

β-CHLORO-PROPYLENE $CH_2:CH.CH_2Cl$ *v.* **Allyl chloride.**

ω-Chloro-propylene $CHCl:CH.CH_3$. *Propenyl chloride.* (36°). Formed, together with some of the following isomeride, by treating propylene chloride with alcoholic KOH (Cahours, *C. R.* 31, 291). Obtained by heating propylidene chloride $CH_3.CH_2.CHCl_2$ with alcoholic KOH (Reboul, *A. Ch.* [5] 14, 462). Formed also by heating the neutral solution of the alkaline salts of the liquid αβ-di-chloro-butyric acid (Wislicenus, *B.* 20, 1010). Liquid. Br at 15° forms $C_3H_5ClBr_2$ (177°). Alcoholic KOH gives allylene. HBr gives $CH_3.CH_2.CHClBr$ (110°) and a small quantity of $CH_3.CHBr.CH_2Cl$ (121°).

Allo-**ω-chloro-propylene** $CHCl:CH.CH_3$. (33°). Formed by heating the neutral solution of the alkaline salts of αβ-di-chloro-butyric acid [63°] (Wislicenus, *B.* 20, 1010).

α-Chloro-propylene $CH_2:CCl.CH_3$. (23°) (O.; L.); (25·5°) (F.). S.G. ^{0} ·9307 (F.); ^{0} ·931 (O.). V.D. 2·83 (calc. 2·65). The chief product of the action of alcoholic KOH on propylene chloride. Formed also by treating $CH_3.CCl_2.CH_3$ (from acetone and PCl_5) with alcoholic KOH, with NH_3, or with AgOAc.

Reactions.—1. H_2SO_4 followed by water gives acetone (Oppenheim, *C. R.* 65, 354; *A. Suppl.* 6, 357).—2. *Water* at 160° also forms acetone.—3. Br gives $CH_2Br.CClBr.CH_3$ (c. 173°) (Friedel, *A. Ch.* [4] 16, 343). 4. Alcoholic KOH at 120° gives allylene (Friedel, *C. R.* 59, 294).—5. HI at 100° gives $CH_3.CClI.CH_3$.—6. Cl in sunshine forms $CH_2Cl.CCl_2.CH_3$ (127°). In the dark Cl forms $CH_2:CCl.CH_2Cl$.—7. HBr gives $CH_3.CBrCl.CH_3$ (93°).—8. HClO gives chloro-acetone (Linnemann, *A.* 138, 122).

αβ-Di-chloro-propylene $CH_2:CCl.CH_2Cl$. (α)-*Epidichlorhydrin.* (α)-*Chloro-allyl chloride.* (94°). S.G. ^{0} 1·236; ^{25} 1·204.

Formation.—1. Together with the following, by the action of Cl on $CH_3.CCl:CH_2$ in the shade (Friedel a. Silva, *C. R.* 73, 957; 74, 806; 75, 81; Fittig, *A.* 135, 359), or of KOH or NEt_3 on $CH_2Cl.CHCl.CH_2Cl$ (Reboul, *A. Suppl.* 1, 229; *C. R.* 95, 993).—2. From $CH_3.CCl_2.CH_2Cl$ and alcoholic KOH (F. a. S.).

Reactions.—1. Br forms $C_3H_4Cl_2Br_2$ (205°).—2. Fuming HCl at 100° gives $CH_3.CCl_2.CH_2Cl$.—3. H_2SO_4 followed by water gives chloro-acetone (Henry, *B.* 5, 186). 4. Alcoholic KOH gives $CH_2.CCl.CH_2OEt$ (110°).—5. ClOH gives *s*-di-chloro-acetone [42°] and $CH_2Cl.CCl_2.CH_2Cl$ (164°) (Henry, *C. R.* 94, 1428).—6. NEt_3 at 100° forms $CH_2:CCl.CH_2NEt_3Cl$ (Reboul, *C. R.* 95, 993).—7. *Sodium* gives allylene and propylene.—8. Alcoholic KCy followed by KOH gives tricarballylic acid and a little oxy-crotonic acid (Claus, *A.* 170, 126).

ωβ-Di-chloro-propylene $CHCl:CH.CH_2Cl$. β-*Epidichlorhydrin.* β-*Chloro-allyl chloride.* (106°) (F. a. S.); (110° cor.) (R.). S.G. $^{15}_{4}$ 1·226 (R.); ^{0} 1·250 (F. a. S.). V.D. 3·83.

Formation.—1. Together with the preceding, by the action of solid KOH on $CH_2Cl.CHCl.CH_2Cl$ (F. a. S.).—2. In the pure state by treating $CH_2Cl.CH(OH).CH_2Cl$ with P_2O_5 (Hartenstein, *J. pr.* [2] 7, 310). 3. A by-product in the action of PCl_5 on acrolein (Geuther, *Z.* 1865, 25; v. Romburgh, *Bl.* [2] 36, 549).

Reactions.—1. Cl gives $CH_2Cl.CHCl.CHCl_2$ (180°).—2. Does not unite with HCl.—3. Alcoholic KOH gives $CHCl:CH.CH_2OEt$ (123°).—4. Aqueous KOH gives β-chloro-allyl alcohol.—5. *Sodium* forms isoallylene $CH_2:C:CH_2$ (Hartenstein).—6. Br gives $CHClBr.CHBr.CH_2Cl$ (212°).

ωα-Di-chloro-propylene $CH_3.CCl:CHCl$. *Allylene dichloride.* (75°) (F. a. S.); (78°) (P. a. K.).

Formation.—1. From $CH_3.CCl_2.CH_2Cl$ by treatment with alcoholic KOH (Friedel a. Silva, *Bl.* [2] 17, 386; *J.* 1872, 322).—2. From tri-chloro-butyric aldehyde and aqueous KOH (Pinner a. Kramer, *A.* 158, 47; 179, 44).

Reactions.—1. Br forms $CH_3.CClBr.CHClBr$ (188°).—2. *Sodium* forms allylene $CH_3.C:CH$.

Di-chloro-propylene $CH_2:CH.CHCl_2$. *Allylidene chloride. Acrolein chloride.* (85° cor.). S.G. $^{21·5}$ 1·170. V.D. 3·83. Formed, together with $CHCl:CH.CH_2Cl$ and $CHCl:CH.CH_2OH$, by the action of PCl_5 on acrolein (Geuther, *A.* 114, 36; *Z.* 1865, 25; v. Romburgh, *Bl.* [2] 36, 549).

Reactions.—1. Cl forms $CH_2Cl.CHCl.CHCl_2$ (180°).—2. KI or CaI_2 at 100° gives C_3H_4ClI (162°) (v. Romburgh, *R. T. C.* 1, 233).—3. Potassium acetate gives $C_3H_4(OAc)_2$ (c. 130°).—

4. *Sodium* has no action.—5. Alcoholic KOH gives CH_2:CH.CHCl(OEt) (c. 118°).—6. NaOEt gives CH_2:CH.$CH(OEt)_2$ (Aronstein, *A. Suppl.* 3, 181). 7. Conc. HClAq at 100° changes it to the isomeric CH_2Cl.CH CHCl. – 8. NH_3 at 100° forms acroleïn-ammonia.

Tri - chloro - propylene $CH_2Cl.CCl:CH_2Cl$. (142°). S.G. $\frac{20}{}$ 1·414. From $CH_2Cl.CCl_2.CH_2Cl$ and alcoholic KOH (Pfeffer a. Fittig, *A.* 135, 361).

Tri-chloro-propylene $CH_3.CCl:CCl_2$. (115°). S.G. $\frac{14}{}$ 1·387. From $CH_3.CCl_2.CHCl_2$ and alcoholic KOH (Borsche a. Fittig, *A.* 133, 117). Cl forms solid $C_3H_3Cl_5$.

Tri-chloro-propylene $C_3H_3Cl_3$. (139°). From the crude product of the chlorination of aldehyde (tri-chloro-butyric aldehyde) and aqueous NaOH (Pinner, *B.* 5, 207). Alcoholic KOH converts it into $C_3H_2Cl_2$.

Tetra-chloro-propylene $C_3H_2Cl_4$. (165°). From $C_3H_4Cl_4$ (derived from acetone) and alcoholic KOH (B. a. F.)

CHLORO-PROPYLENE GLYCOL *v.* GLYCERIN *chlorhydrin.*

CHLORO-PROPYLIDENE CHLORIDE *v.* TRI-CHLORO-PROPANE.

CHLORO-DI-ISOPROPYL-KETONE $C_3H_7.CO.C_3H_6Cl$. (142°). Prepared by passing Cl into di-iso-propyl-ketone at 0° (Barbaglia a. Gucci, *B.* 13, 1570; *G.* 11, 92). Liquid.

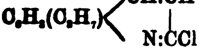
Di-chloro-di-isopropyl-ketone $C_6H_{12}Cl_2$:CO. (176°). Prepared by passing chlorine into di-isopropyl-ketone at the ordinary temperature (B. a. G.). Colourless liquid. Turpentine-like odour.

Tri-chloro-di-isopropyl-ketone $C_6H_{11}Cl_3$:CO. (about 229°). Prepared by passing Cl into boiling di-isopropyl-ketone (B. a. G.). Liquid with pungent turpentine-like odour.

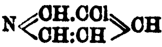
CHLORO-ISOPROPYL NITRATE $CH_3.CH(NO_3).CH_2Cl$. (158°). S.G. $\frac{12}{}$ 1·28. From chloro-isopropyl alcohol HNO_3, and H_2SO_4 (Henry, *A. Ch.* [4] 27, 263).

αβ-Di-chloro-propyl nitrate $CH_2Cl.CHCl.CH_2NO_3$. (180°). S.G. $\frac{7}{}$ 1·3. From $CH_2Cl.CHCl.CH_2OH$ and HNO_3 (Henry, *B.* 7, 409).

Di-chloro-isopropyl nitrate $(CH_2Cl)_2CH.NO_3$. (180°–190°). S.G. $\frac{10}{}$ 1·465. Formed from $CH_2Cl.CH(OH).CH_2Cl$, HNO_3, and H_2SO_4 (Henry, *A.* 155, 167).

(*Py.* 3)-CHLORO-(*B.* 3)-ISOPROPYL QUINOLINE  $C_6H_3(C_3H_7)\left<\begin{matrix}CH:CH\\ |\\ N:CCl\end{matrix}\right.$ *Chloro-cumoquinoline.* Formed by heating isopropyl-carbostyril with PCl_5 (Widmann, *B.* 19, 265). Yellowish oil. Heavier than water. V. sol. alcohol, ether, benzene, &c., nearly insol. water. Sparingly volatile with steam. Weak base.—$B'_2H_2Cl_2PtCl_4$: [138°]; yellow monoclinic prisms.

CHLORO-PYRENE *v.* PYRENE.

CHLORO - PYRIDINE C_5H_4ClN *i.e.*  $N\left<\begin{matrix}CH.CCl\\ CH:CH\end{matrix}\right>CH$. (148°). V.D. 57 (obs.).

Formation.—1. By heating potassium pyrrol with chloroform in presence of ether; the residue after evaporation of the ether is boiled with dilute HCl to resinify the unaltered pyrrol, and after making alkaline with KOH, the chloropyridine is distilled over with steam (Ciamician a. Dennstedt, *G.* 11, 221, 300; *B.* 14, 1153).—2. By the action of CCl_4, chloral, or tri-chloroacetic ether on pyrrol-potassium (Ciamician a. Dennstedt, *B.* 15, 1179).—3. From oxy-pyridine and PCl_3 (Lieben a. Haitinger, *M.* 6, 315).

Properties.—Pungent alkaline liquid; m. sol. water.

Reactions.—1. HI at 145° gives iodo-pyridine; at 200° it forms pyridine (L. a. H.) – 2. Br and I form additive compounds. – 3. *Sodium amalgam* forms chloro-piperidine $C_5H_{10}ClN$.

Salts. — B'HCl: deliquescent crystals. — $B'_2H_2PtCl_6$aq: monoclinic needles; *a*:*b*:*c* = 1·197:1:1·172; β = 109° 48′ (C. a. D.); *a*:*b*:*c* = 1·04:1:1·25; β = 72° 42′ (L. a. H.). Converted by heat into B'_2PtCl_4.

Hexahydride $C_5H_{10}ClN$. *Chloropiperidine.* From chloro-pyridene by reduction with sodium amalgam or with Zn and HCl.—$B'_2H_2PtCl_6$aq: monoclinic needles; *a*:*b*:*c* = 1·209:1:1·094; β = 113° 35′.

Di-chloro-pyridine $C_5H_3Cl_2N$. [67°]. Formed by heating barium pyridine-di-sulphonate with PCl_5 (Koenigs a. Geigy, *B.* 17, 1833). Volatile with steam. Glistening plates. V. sol. alcohol, sl. sol. water. $HgCl_2$ added to the aqueous or alcoholic solution precipitates a double salt which forms long fine needles [183°]. — $B'_2H_2Cl_2PtCl_4$ 2aq: fine yellow needles.

Di-chloro-pyridine $C_5H_3Cl_2N$. [72°]. Formed, together with other products, by the action of dry chlorine upon dry pyridine. Slender white needles; sol. pyridine and alcohol, insol water. Has an agreeable aromatic odour (Keiser, *Am.* 8, 308).

Tri-chloro-pyridine $C_5H_2Cl_3N$. [50°]. Formed, together with di-chloro-pyridine [67°] by heating barium pyridine-di-sulphonate with PCl_5 (Koenigs a. Geigy, *B.* 17, 1832). Volatile with steam. Long flat needles. Sol. alcohol, nearly insol. water.

Tri-chloro-pyridine (?) $C_5H_2Cl_3N$. [65°]. Formed, along with chloro-oxy-pyridine carboxylic acid (*q. v.*) by treating nicotinic acid with PCl_5, and warming the product with H_2SO_4 (80 p.c.) (Seyfferth, *J. pr.* [2] 34, 261). Long needles (by sublimation); v. sl. sol. water, sol. alcohol, ether, and benzene.

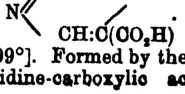
CHLORO-PYRIDINE-CARBOXYLIC ACID $C_6H_4ClNO_2$ *i.e.* $C_5H_3ClN.CO_2H$. *Chloro-picolinic acid.* [180°]. From picolinic acid by treatment with PCl_5, the resulting chloro-picolines, including $C_5H_3ClNCCl_3$, being warmed with H_2SO_4 (80 p.c.) (Seyfferth, *J. pr.* [2] 34, 249).

Properties.—Dendritic needles or prisms, sl. sol. cold water; extracted by ether from aqueous solution.

Salts. CaA'_2 aq.

Reaction.—I. HI reduces it to picolinic acid; in presence of phosphorus, picoline is also formed.

Chloro-pyridine carboxylic acid $C_5H_3NCl.CO_2H$. [168°]. *Chloro-picolinic acid.* From di-chloro-pyridine carboxylic acid, HOAc, and HI at 150° (Ost, *J. pr.* [2] 27, 284). Needles or prisms (containing aq).—BaA'_2 2aq.

Chloro-pyridine-carboxylic acid $C_5H_3NCl.CO_2H$ *i.e.*  $N\left<\begin{matrix}CCl.CH:CH\\ /\\ CH:C(CO_2H)\end{matrix}\right.$. *Chloro-nicotinic acid.* [199°]. Formed by the action of PCl_5 on oxy-pyridine-carboxylic acid [303°]

(Pechmann a. Welsh, *B.* 17, 2392; *C. J.* 47, 145). Sublimable. Glistening plates. Sol. water, alcohol, ether, and acetic acid, sl. sol. benzene. By tin and HCl it is reduced to nicotinic acid.

Di-chloro-pyridine carboxylic acid $C_5H_2NCl_2.CO_2H$. *Di-chloro-nicotinic acid.* [138°]. One of the products of the action of warm H_2SO_4 (80 p.c.) on the oily product got from nicotinic acid and PCl_5 (Seyfferth, *J. pr.* [2] 34, 262). Clumps of needles (from water).

Ethyl ether EtA'. [50°].

Di-chloro-pyridine carboxylic acid $C_5H_2Cl_2N.CO_2H$. *Di-chloro-picolinic acid.* [180°].

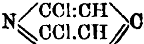
Preparation.—The mixture of penta- and hexa-chloro-picolines obtained by boiling (10 g.) comenamic acid with (20 g.) dilute (80 p.c.) H_2SO_4 for an hour contains dichloro-, dichloroxy-, and chloroxy-picolinic acids. The first acid is extracted by chloroform, the other two are separated by means of their lime salts, the calcic chloroxy-picolinate being the more soluble (Ost, *J. pr.* [2] 27, 281). *Properties.*—Slender needles (containing aq); sl. sol. cold water, v. sol. hot water and chloroform. Gives no odour with Fe_2Cl_6. Reduced by HI in glacial acetic acid to picolinic acid.

Salts. NaA'. Trapezoidal plates.—KA'. Triangular and trapezoidal plates, often twins.

Tetra-hydride $C_5H_7ClN.CO_2H$. [c. 268°]. From the above by tin and HCl. Laminæ (from water).—B'HCl.

Di-chloro-pyridine-carboxylic acid

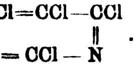
$C_5H_2N(Cl)_2(CO_2H)$ *i.e.*



$N\begin{matrix}\diagup CCl:CH \diagdown \\ \diagdown\!\!\diagdown CCl.CH \diagup\!\!\diagup\end{matrix}C.CO_2H$ (?).

[210°]. Formed by heating citrazinic acid with PCl_5 (Behrmann a. Hofmann, *B.* 17, 2694). Colourless plates Sol. alcohol, v. e. sol. ether, sl. sol. water. A'Ag: colourless needles.

TETRA-CHLORO-PYRIMIDINE $C_4N_2Cl_4$ *i.e.*



$$\begin{matrix}CCl{=}CCl{-}CCl \\ | \qquad\quad\;\; \| \\ N{=}CCl{-}N\end{matrix}$$

. [68°]. Formed by heating alloxan (1 pt.) with PCl_5 (6 pts.) and $POCl_3$ (5 pts.) for 8 hrs. at 120°-130°. Colourless pearly plates, of camphor-like smell. Volatile with steam (Ciamician a. Magnaghi, *G.* 16, 173; *B.* 18, 3445).

TETRA-CHLORO-PYROCATECHIN $C_6Cl_4(OH)_2$ [1:2:3:4:5:6]. [174°]. Obtained by passing chlorine into a hot, strong solution of pyrocatechin in acetic acid. Colourless needles or thick plates. On oxidation it gives tetra-chloro-*o*-quinone $C_6Cl_4O_2$ (Zincke, *B.* 20, 1779)

PER-CHLORO-PYROCOLL $C_{10}N_2O_2Cl_6$. [above 320°]. Formed, together with the tetra-chloride, by heating pyrocoll (1 g.) with PCl_5 (12 g.) at 220° for 6 hrs. (Ciamician a. Danesi, *G.* 12, 31). Scales. Insol. cold HOAc. Changed by long boiling into tri-chloro-pyrrol carboxylic acid.

Tetra-chloride $C_{10}N_2O_2Cl_{10}$. Formed as above (C. a. D.). Pearly triclinic prisms (from HOAc). Sl. sol. cold HOAc.

Octo-chloride $C_{10}N_2O_2Cl_{14}$. [147°]. From per-chloro-pyrocoll and PCl_5 at 250°. Sublimes a little above 100°. Smells like camphor. By reduction with zinc-dust and acetic acid it yields tetra-chloro-pyrrol. Heated with water at about 130° it decomposes into (α)-di-chloro-acrylic acid [86°], NH_3, CO_2, and HCl. By boiling with dilute acetic acid it is resolved into di-chloro-maleimide, CO_2 and HCl (Ciamician a. Silber, *G.* 13, 320; *B.* 16, 2389).

TRI-CHLORO-PYROGALLOL $C_6Cl_3(OH)_3$. *Tri-chloro-pyrogallic acid.* [c. 185°] (H. a. S.). A mixture of pyrogallol (5 g.) and acetic acid (12·5 c.c. of 60 p.c.) is kept cool and dry chlorine is passed in. In half-an-hour tri-chloro-pyrogallol crystallises out (Webster, *C. J.* 45, 205).

Properties. Fine needles (containing 3aq). Resembles tri-bromo-pyrogallol, notably in giving a deep blue colour when baryta is added to its ethereal solution. When anhydrous it melts about 177° (W.); when hydrated it melts at 115° (W.) or 75° (H. a. S.). Sol. water, but slowly decomposed by it. Sol. acetic acid, benzene, chloroform, CS_2, and CCl_4. V. sol. alcohol and ether. Reduces ammoniacal $AgNO_3$ to a mirror.

Reactions.—1. *Sodium sulphite* gives a fugitive red colour.—2. Conc. HNO_3 decomposes it. 3. Treated with chloroform saturated with chlorine, it turns wine-red, then effervesces and becomes yellow. On evaporation, crystals of 'leucogallol,' $C_{18}H_6Cl_6O_{12}$ 2aq (Stenhouse a. Groves, *C. J.* 28, 704), separate. Hence pyrogallol added to chloroform saturated with chlorine is converted into 'leucogallol,' the intermediate tri-chlorinated body being found to very small extent.

Salts. — $Ba_3(C_6Cl_3O_3)_2$ 6aq (Hantzsch a. Schniter, *B.* 20, 2033).—$Cu_3(C_6Cl_3O_3)_2$ 6aq.

Acetyl derivative $C_6Cl_3(OAc)_3$. [122°]. Needles.

βγ-DI-CHLORO-PYROMUCIC ACID $C_5H_2Cl_2O_3$ [169°]. Obtained by the action of conc. alcoholic KOH upon pyromucic-ether-tetra-chloride (formed by combination with chlorine in the cold) (Denaro, *G.* 16, 333; Hill a. Jackson, *B.* 20, 252). Felted needles. Sol. hot water, v. sol. alcohol and ether, m. sol. boiling benzene or chloroform, sl. sol. cold benzene or chloroform. Warmed with excess of bromine-water it is converted into mucochloric acid with evolution of CO_2. By boiling with dilute HNO_3 (1:2) it yields mucochloric acid and di-chloro-maleic acid.

Salts.—A'_2Ba 3aq: fine needles, sl. sol. cold water.—A'_2Ca 4aq: long needles, sl. sol. cold water.—A'K: rather sparingly soluble small prisms.—A'Ag: fine needles.

Ethyl ether A'Et: [64°], slender needles.

Amide $C_4HCl_2O.CO.NH_2$: [176°], felted needles.

CHLORO-PYROTARTARIC ACIDS.

Ita-chloro-pyrotartaric acid $C_5H_7ClO_4$. [140°-145°]. (c. 230°). From itaconic acid and conc. HCl at 130° (Swarts, *Z.* 1866, 721). In a current of dry air at 150° it forms an anhydride. Boiling water or alkalis form paraconic acid, $C_5H_6O_4$, which rapidly changes to itamalic acid, $C_5H_8O_5$.

Diethyl ether Et_2A''. (251°).

Citra-chloro-pyrotartaric acid $C_5H_7ClO_4$. [129°]. From citraconic anhydride and cold fuming HCl. Formed also by the union of mesaconic acid with HCl (Fittig, *A.* 188, 51). Tables. Boiling water splits it up into HCl and mesaconic acid. Boiling alkalis form methacrylic acid.

Ita-di-chloro-pyrotartaric acid $C_5H_6Cl_2O_4$. (S.).

Citra-di-chloro-pyrotartaric acid $C_5H_6Cl_2O_4$. From citraconic acid and Cl (Swarts, *J.* 1873, 582; *Bull. Acad. Roy. Belg.* [2] 33, No. 1). On distillation it gives HCl and citraconic anhydride. Boiling water converts it into chloro-citramalic acid $C_5H_7ClO_3$. The Na salt when boiled in aqueous solution gives chloro-methacrylic acid.

TETRA-CHLORO-PYRROL C_4Cl_4NH. [110°]. (261°) at 754 mm.

Formation.—1. Together with di-chloro-maleic acid and NH_3, by treating pyrrol with NaOCl. — 2. By reduction of per-chloro-pyrocoll-octo-chloride with zinc-dust and acetic acid. 3. By heating di-chloro-maleïmide with PCl_5 at 160°.—4. By reducing with zinc-dust and HCl the per-chloride C_4Cl_7N which is obtained by heating di-chloro-maleïmide with PCl_5 at 200° (Ciamician a. Silber, *B.* 16, 2390; 17, 551, 1743; *G.* 14, 356). Very volatile. Long silky plates. V. sol. alcohol and ether, sl. sol. water. Dissolves in alkalis. The ammoniacal solution gives a white pp. with $AgNO_3$. It dissolves in strong H_2SO_4 with an intense reddish-brown colour; on adding a few drops of water this changes to violet, and by further addition of water gives a green pp. which dissolves in KOH with an intense orange colour.

(*α*)-**TRI-CHLORO-PYRROL-CARBOXYLIC ACID** $C_5Cl_3H_2NO_2$ *i.e.* $C_4HCl_3N.CO_2H$.

Prepared by heating per-chloro-pyrocoll with caustic potash.

$$C_{10}Cl_6N_2O_2 + 2KOH = 2C_4Cl_3HNCO_2K$$

(Ciamician a. Danesi, *G.* 12, 34). Long silky needles (containing aq). V. sol. alcohol and ether, sl. sol. water; its solutions give with lead acetate a white pp., and with ferric chloride an intense red colouration. It decomposes with violence at 150°. BaA'_2aq: scales, m. sol. alcohol, sl. sol. water.

TRI-CHLORO-PYRUVIC ACID *Hydrate* $CCl_3.C(OH)_2.CO_2H$. *Tri-chloro-isoglyceric acid.* [102°]. Prepared by saponification of tri-chloro-acetyl cyanide with HCl (Claisen a. Antweiler, *B.* 13, 1937). Formed also, together with tri-carballylic acid, by treating gallic acid, salicylic acid, or phenol with HCl and $KClO_3$ (Schreder, *A.* 177, 282). Colourless prisms. V. sol. water, alcohol, ether, acetic acid, and acetone; m. sol. C_6H_6 and CS_2; insol. petroleum ether. Reduces Fehling's solution and ammoniacal $AgNO_3$. Warmed with an alkali it readily splits up into chloroform and an oxalate.—$A''Ba$: small soluble prisms.—$NaA'xaq$ (Hofferichter, *J. pr.* [2] 20, 198).

Amide $CCl_3.C(OH)_2.CONH_2$. [127°]. Prepared by the action of cold aqueous HCl on tri-chloro-acetyl cyanide. Colourless crystals. Sol. water, alcohol, ether, and acetone; sl. sol. CS_2, C_6H_6, and $CHCl_3$. On heating it loses H_2O and is converted into a compound of the formula $C_3Cl_3O_2H_2N$, which forms small plates or needles of melting-point [218°], which are sublimable and sol. ether, sl. sol. water.

Nitrile *v.* TRI-CHLORO-ACETYL CYANIDE.

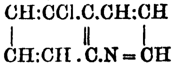
ω-**CHLORO-PYRUVIC ALDEHYDE** $CH_2.CO.CClO$.

Oxim $CH_3.CO.CCl(NOH)$: *v.* CHLORO-ISONITROSO-ACETONE.

CHLORO-QUARTENYLIC ACID *v.* CHLORO-CROTONIC ACID.

DI-CHLORO-QUINALDINE *v.* DI-CHLORO-(*Py.* 3)-METHYL-QUINOLINE.

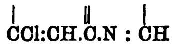
(*B.* 1)-**CHLORO-QUINOLINE** C_9H_6ClN *i.e.*



$$\begin{array}{llll}\mathrm{CH{:}CCl.} & \mathrm{C.} & \mathrm{CH{:}} & \mathrm{CH}\\ | & \| & & | \\ \mathrm{CH{:}CH\,.} & \mathrm{C.} & \mathrm{N=} & \mathrm{CH}\end{array}$$

[32°]. (268°). Formed together with the (*B.* 3)-isomeride by heating *m*-chloro-aniline with glycerin, nitrobenzene, and H_2SO_4 (La Coste, *B.* 18, 2940). Formed also from the corresponding amido-quinoline by Sandmeyer's reaction (Freydl, *M.* 8, 583). Needles or thick glistening prisms. The bichromate forms long yellow needles, [165°]; sol. hot water, sl. sol. cold.

(*B.* 3)-**Chloro-quinoline**



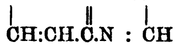
$$\begin{array}{llll}\mathrm{CH{:}CH.} & \mathrm{C.} & \mathrm{CH{:}} & \mathrm{CH}\\ | & \| & & | \\ \mathrm{CCl{:}CH.} & \mathrm{C.} & \mathrm{N\,:} & \mathrm{CH}\end{array}$$

(c. 257°). Formed, together with the (*B.* 1)-isomeride, by heating *m*-chloro-aniline with glycerine, nitrobenzene, and H_2SO_4. Liquid; solidifies in a freezing mixture. Volatile with steam. V. sol. alcohol, ether, and benzene; nearly insol. water. Is probably not quite pure (La Coste, *B.* 18, 2940).

Salts. — $B'HCl$: colourless tables. $B'_2H_2Cl_2PtCl_4 2aq$: orange silky needles. $B'_2H_2Cr_2O_7$: [119°] fine yellow silky needles; S. ·25.

Methylo-iodide $B'MeI$: [232°]; long yellow needles. On oxidation with $KMnO_4$ it gives the formyl-derivative of chloro-methyl-amido-benzoic acid, and chloro-methyl-isatin (La Coste a. Bodewig, *B.* 17, 926; 18, 428).

(*B.* 2)-**Chloro-quinoline**



$$\begin{array}{llll}\mathrm{CCl{:}CH.} & \mathrm{C.} & \mathrm{CH{:}} & \mathrm{CH}\\ | & \| & & | \\ \mathrm{CH{:}CH.} & \mathrm{C.} & \mathrm{N\,:} & \mathrm{CH}\end{array}$$

(256°). Prepared by heating *p*-chloraniline with glycerine, nitro-benzene, and H_2SO_4; the yield is 100 p.c. (La Coste, *B.* 15, 560). Colourless liquid.

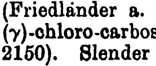
Salts.—BHCl: soluble colourless needles. $(BHCl)_2PtCl_4 2aq$: yellow crystalline pp.

Methylo-iodide $B'MeI$: soluble crystalline solid.—$(BMeCl)_2PtCl_4$: orange crystalline pp.

(*Py.* 3)-**Chloro-quinoline** C_9H_6NCl. [38°]. (267°). Formed by the action of PCl_5 on carbostyril or oxy-carbostyril (Friedländer a. Ostermayer, *B.* 15, 333). Volatile with steam. Long needles. V. sol. alcohol, ether, benzene and ligroin, nearly insol. water. On heating with water to 120° it gives carbostyril.

Chloro-quinoline C_9H_6ClN. Formed by heating cynurin with PCl_5 and $POCl_3$ (Kretschy, *M.* 2, 77).—$B'H_2PtCl_6 2aq$.

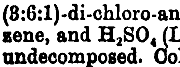
(*Py.* 1,3)-**Di-chloro-quinoline**, called (*γ*),



$$C_6H_4\left\langle\begin{array}{l}\mathrm{CCl{:}CH}\\ \quad\quad\ |\\ \mathrm{N\ :\ CCl}\end{array}\right.$$

[67°]. (281°). Formed by the action of PCl_5 on (*Py.* 1,3)-di-oxy-quinoline (Friedländer a. Weinberg, *B.* 15, 2683) or on (*γ*)-chloro-carbostyril (Baeyer a. Bloem, *B.* 15, 2150). Slender needles; sol. alcohol, ether, and benzene, nearly insol. water.

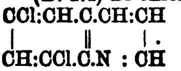
(*B.* 1:4)-**Di-chloro-quinoline**



$$\begin{array}{llll}\mathrm{CH{:}CCl.} & \mathrm{C.} & \mathrm{CH{:}} & \mathrm{CH}\\ | & \| & & | \\ \mathrm{CH{:}CCl.} & \mathrm{C.} & \mathrm{N=} & \mathrm{CH}\end{array}$$

[93°]. Prepared by heating (3:6:1)-di-chloro-aniline with glycerin, nitro-benzene, and H_2SO_4 (La Coste, *B.* 15, 561). Volatile undecomposed. Colourless needles or tables. Sol. alcohol and ether.

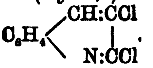
(*B.* 2:4)-Di-chloro-quinoline



$$\begin{array}{l}\mathrm{CCl{:}CH.C.CH{:}CH}\\ |\qquad\quad \|\qquad\quad |\\ \mathrm{CH{:}CCl.C.N : CH}\end{array}$$

. [104°]. **Prepared by heating** (4:2:1)-di-chloro-aniline with glycerin, nitro-benzene, and H_2SO_4 (La Coste, *B.* 15, 561). Long fine colourless needles. Sl. sol. alcohol.

(*Py.* 2,3)-**Di-chloro-quinoline** $C_9H_5Cl_2N$ *i.e.*



$$C_6H_4\left\langle\begin{array}{l}\mathrm{CH{:}CCl}\\ \qquad |\\ \mathrm{N{:}CCl}\end{array}\right.$$

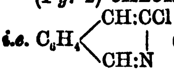
. [105°]. Weak base. Prepared by treating hydro-carbostyril with PCl_5 and distilling the product with steam; the yield is 20-30 p.c. (Baeyer, *B.* 12, 1320). Insol. water, sol. alcohol, ether, and C_6H_6. On reduction with HI it gives quinoline.

Tri-chloro-quinoline $C_9H_4Cl_3N$. [108° uncor.]. Formed by heating phenyl-malonamic acid (malonanilidic acid) $CO_2H.CH_2.CO.NHPh$ with benzene and PCl_5 (Rügheimer, *B.* 17, 736). Long colourless needles. Volatile with steam. Sol. alcohol, benzene, and ligroin. By heating with an acetic acid solution of HI at 210° it is reduced to quinoline.

Tri-chloro-quinoline $C_9H_4Cl_3N$. [161°]. From di-chloro-carbostyril and PCl_5 (Friedländer a. Weinberg, *B.* 15, 1425). Slender needles (from alcohol); slightly volatile with steam.

Tri-chloro-quinoline $C_9H_4Cl_3N$. [211°]. Formed by acting on the borate of (*B.* 4)-chloro-quinoline with bleaching powder solution (Emhorn and Lauch, *A.* 243, 361). Needles (from acetic ether).

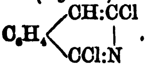
(*Py.* 2)-**CHLORO-ISOQUINOLINE** C_9H_6ClN *i.e.*



$$C_6H_4\left\langle\begin{array}{l}\mathrm{CH{:}CCl}\\ \qquad\quad |\\ \mathrm{CH{:}N}\end{array}\right.$$

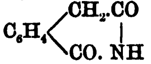
(?). [45°-48°]. (280°) at 753 mm. Formed by heating the di-chloro-derivative [123°] with HI and P at 170°. By more prolonged action at 200° it is completely di-chlorinated to isoquinoline. Long colourless needles. Weak base (Gabriel, *B.* 19, 1655, 2356).

(*Py.* 2:4)-**Di-chloro-isoquinoline** $C_9H_5Cl_2N$ *i.e.*



$$C_6H_4\left\langle\begin{array}{l}\mathrm{CH{:}CCl}\\ \qquad\ |\\ \mathrm{CCl{:}N}\end{array}\right.$$

. [123°]. (306°). Formed by heating the imide of phenyl-acetic-*o*-carboxylic acid



$$C_6H_4\left\langle\begin{array}{l}\mathrm{CH_2.CO}\\ \qquad\quad |\\ \mathrm{CO.\ NH}\end{array}\right.$$

with $POCl_3$ (8 pts.) at 150°-170°. Very long flat needles (from alcohol). V. sol. chloroform, benzene, ether, and hot alcohol. Slowly volatilises with steam. By HI and P it is first reduced to the mono-chloro-derivative and finally to isoquinoline (Gabriel, *B.* 19, 1655, 2355).

CHLORO-QUINONE $C_6H_3ClO_2$. **[57°].**

Formation.—1. By distilling cupric quinate (25 g.) with NaCl (60 g.), MnO_2 (40 g.), H_2SO_4 (100 g.), and water (170 g.) (Städeler, *A.* 69, 300). 2. By oxidation of chloro-hydroquinone with CrO_3 (Levy a. Schultz, *A.* 210, 144; *B.* 13, 1428). 3. By adding aqueous K_2CrO_4 to a slightly acid solution of chloro-amido-phenol sulphate (Kollrepp, *A.* 234, 14).

Properties.—Long yellow trimetric needles; $a:b:c = \cdot47:1:1\cdot71$; v. sol. ether, m. sol. alcohol, HOAc, and hot water. Turns the skin purple. Reduced by SO_2 to chloro-hydroquinone.

Reactions.—1. When mixed with *m-nitro-aniline* in benzene solution, dark green crystals of $C_6H_3Cl(O)_2(NH_2.C_6H_4.NO_2)_2$ separate. This breaks up into its constituents even on recrystallising from benzene (Niemeyer, *A.* 228, 322). 2. *p-Toluidine* forms, in the same way, white plates [90°] (×$C_6H_3Cl(OH)_2(C_7H_9N)_2$?)

(*α*)-**Di-chloro-quinone** $C_6H_2Cl_2O_2$ [5:2:4:1]. [159°].

Formation.—1. One of the products of the distillation of cupric quinate with MnO_2, NaCl, and H_2SO_4 (Städeler, *A.* 69, 300).—2. From benzene and Cl_2O (Carius, *A.* 143, 315).—3. Together with chloro-benzene and tri-chloro-phenomalic acid, by dissolving benzene (48 g.) in H_2SO_4 (300 g.), diluting with water (150 g.), and, after cooling, adding more benzene (100 g.) and $KClO_3$ (150 g.). The mixture is left to itself for a week (C.).—4. By the oxidation of (*α*)-di-chloro-hydroquinone with conc. HNO_3 (Levy a. Schultz, *B.* 13, 1428; *A.* 210, 150).—5. By oxidation of di-chloro-*p*-phenylene-diamine [164°] with $K_2Cr_2O_7$ and H_2SO_4 (Möhlau, *B.* 19, 2010).—6. By oxidation of *p*-di-chloro-aniline with $K_2Cr_2O_7$ and H_2SO_4.—7. From quinone by two alternate treatments with HCl and with Fe_2Cl_6 (Levy, *B.* 18, 2366).—8. By adding K_2CrO_4 to a solution of di-chloro-amido-phenol sulphate (Kollrepp, *A.* 234, 15).

Properties. — Yellow monoclinic crystals; $a:b:c = 1\cdot15:1:2\cdot21$; $\beta = 56°\ 26'$ (Grunling); $a:b:c = 1\cdot09:1:1\cdot84$; $\beta = 89°\ 11'$ (Fock, *Z. K.* 7, 40). Sol. ether and chloroform, nearly insol. alcohol, insol. water. Volatile with steam. SO_2 reduces it to di-chloro-hydroquinone [172°].

Reactions.—1. *Aniline* in acetic acid solution, in presence of some HCl, forms blue plates of the **anilide** $C_6HCl_2O_2(NPhH)$ [5:2:4:1:3] [180°], which dissolves in conc. H_2SO_4 giving a deep-blue liquid (Niemeyer, *A.* 228, 332).—2. If, after warming with aniline, the hot solution is treated with HOAc, lustrous brown plates of the **di-anilide** $C_6Cl_2O_2(NPhH)_2$ [290°] are formed. This is the so-called 'chloranil-anilide' obtained from tetra-chloro-quinone and aniline.—3. *m-Nitro-aniline* forms dark green crystals of $C_6H_2Cl_2O_2(NH_2.C_6H_4.NO_2)_2$ [110°] which may be crystallised from hot benzene (Niemeyer, *A.* 228, 322).—4. *p-Toluidine* forms a crystalline compound [115°] (×$C_6H_2Cl_2O_2(C_7H_9N)_2$?).

(*β*)-**Di-chloro-quinone** $C_6H_2Cl_2O_2$ [2:6:1:4]. [120°].

Formation.—1. By oxidation of trichlorophenol with HNO_3, or a mixture of HNO_3 and H_2SO_4 (Faust, *Z.* 1867, 727; Weselsky, *B.* 3, 646; Levy a. Schultz, *B.* 13, 1428; Guareschi a. Daccomo, *B.* 18, 1170).—2. In small quantity by treating di-chloro-nitro-phenol [125°] with HNO_3 and H_2SO_4 (Armstrong, *Z.* 1871, 521).—3. By oxidation of di-chloro-*p*-phenylene-diamine with CrO_3 (Levy, *B.* 16, 1445). Yellow trimetric crystals, $a:b:c = \cdot7127:1:2\cdot027$. V. sol. boiling alcohol, v. sl. sol. hot water. Turns the skin brown. Readily sublimes. Volatile with steam. SO_2 forms (*β*)-di-chloro-hydroquinone [158°].

Reactions.—1. *Aniline* (1 mol.) in alcoholic solution containing a little HCl, forms bluish-violet needles or plates of the **anilide** $C_6HCl_2O_2(NPhH)$ [154°]. This is sol. alcohol and ether, and gives a violet-blue solution in conc. H_2SO_4 (Niemeyer, *A.* 228, 332).—2. Excess of *aniline* added to an alcoholic or acetic acid solution forms $C_6HClO_2(NPhH)_2$ [2:1:4:6:3] [262°]. This forms lustrous brown plates, sl. sol. alcohol and benzene, m. sol. hot HOAc (N.).—3. *m-Nitro-aniline* forms glittering dark green prisms of $C_6H_2Cl_2O_2(NH_2.C_6H_4.NO_2)_2$ [112°]. -4. *p-Toluidine* forms, in the same way, slender needles [73°] ($^*C_6H_2Cl_2(OH)_2C_7H_9N$?).

Tri-chloro-quinone $C_6HCl_3O_2$. [163°].

Formation. —1. By chlorinating quinone (Woskresensky, *J. pr.* 18, 419). 2. By boiling quinic acid with MnO_2 and HCl (Städeler, *A.* 69, 318). 3. Together with tetrachloroquinone, by treating phenol with $KClO_3$ and aqueous HCl (Graebe, *A.* 146, 9; Stenhouse, *C. J.* 21, 141).—4. From benzene and CrO_2Cl_2 (Carstanjen, *B.* 2, 633).—5. By dropping sodium hypobromite solution slowly into a solution of the hydro-chloride of tri-chloro-*p*-amido-phenol; the pp. is re-crystallised from alcohol (M. Andresen, *J. pr.* [2] 28, 422).—6. From *p*-amido-phenol (*q. v.*) and bleaching powder (Schmitt a. Andresen, *J. pr.* [2] 23, 436).

Properties. —Yellow prisms. May readily be sublimed. Does not colour the skin. Insol. water, sol. hot alcohol, v. sol. ether. Dilute aqueous KOH dissolves it, forming di-chloro-di-oxy-quinone (chloranilic acid).

Reactions. 1. With alcoholic solution of *aniline* it gives glittering plates of di-chloro-quinone-di-anilide: $2C_6HCl_3O_2 + 3PhNH_2 = C_6(NPhH)_2Cl_2O_2 + C_6HCl_3(OH)_2 + PhNH_2HCl$. This substance crystallises from benzene in tablets which have a bluish lustre (M. Andresen, *J. pr.* [2] 28, 423).—2. *Aniline* (1 mol.) forms lustrous leaflets of $C_6HClO_2(NPhH)_2$. This forms a blue solution in conc. H_2SO_4 (Schultz, *B.* 10, 1792; *A.* 210, 180). 3. *Aniline* treated with excess of the quinone forms blue plates of $C_6Cl_3O_2(NPhH)$ (Niemeyer, *A.* 228, 332). 4. *m-Nitro-aniline* forms lustrous dark-green prisms of $C_6HCl_3O_2(NH_2.C_6H_4.NO_2)_2$ [108°] (N.). -5. PCl_5 at 190° gives C_6Cl_6.—6. AcCl gives the di-acetyl derivative of tetra-chloro-hydroquinone. -7. Boiling conc. aqueous HCl forms tetra-chloro-hydroquinone.

Tetra-chloroquinone $C_6Cl_4O_2$.

Formation.—1. By the action of a mixture of $KClO_3$ and HCl on quinone, aniline, phenol, tri-chloro-phenol, di-nitro-phenol, tri-nitro-phenol, salicin, salicylic acid, isatin, quinic acid, tyrosine, *m*-amido-benzoic acid, &c. (Hofmann, *A.* 52, 55; Hesse, *A.* 114, 303; Staedeler, *A.* 69, 326; 116, 99; Stenhouse, *A.* 78, 4; *A. Suppl.* 6, 209; Erlenmeyer, *J.* 1861, 404; *N. Jahr. Pharm.* xvi. 292). 2. By passing chlorine into an alcoholic solution of chloro-isatin (Erdmann, *A.* 48, 309).—3. From penta-chloro-phenol and fuming HNO_3 (Merz a. Weith, *B.* 5, 460).—4. Prepared by oxidation of tetrachlorohydroquinone (Levy a. Schultz, *B.* 13, 1429).—5. By heating trichloroquinone (5 g.) for 12 hours with fuming HCl (100 c.c.). The product is oxidised by strong HNO_3 and recrystallised from alcohol (Andresen, *J. pr.* [2] 28, 425).—6. From *s*-tetra-chloro benzene [137°] and fuming HNO_3 (Beilstein a. Kurbatoff, *A.* 192, 286).—7. From phenol and chloride of iodine (Stenhouse, *C. J.* 23, 6). -8. From di-chloro-di-oxy-quinone and PCl_5.

Properties.—Pale yellow lustrous scales. Monoclinic; $a:b:c = 1{\cdot}52:1:3{\cdot}00$; $\beta = 73°56'$ (Fork, *Z. K.* 7, 40). When heated gently it sublimes without melting. Insol. water, v. sl. sol. cold alcohol, m. sol. ether. Not attacked by HNO_3, by HCl, or by boiling conc. H_2SO_4. SO_2 reduces it to tetra-chloro-hydroquinone. Boiling HCl or HBr also reduce it to the same body.

Reactions.—1. Conc. aqueous $KHSO_3$ forms 'potassium thiochronate' $C_6(OH)O_2(SO_4K)(SO_3K)_2$. Dilute $KHSO_3$ gives $C_6Cl_2(OH)_2(SO_3K)_2$. -2. Aqueous KOH forms a purple solution containing $C_6Cl_2(OK)_2O_2$.—3. AcCl at 170° gives Cl and $C_6Cl_4(OAc)_2$ (Graebe, *A.* 146, 12).- 4. PCl_5 at 180° gives C_6Cl_6. -5. Aqueous NH_3 gives $C_6Cl_2(NH_2)(OH)O_2$ (Erdmann, *J. pr.* 22, 287; Laurent, *A. Ch.* [3] 3, 493). 6. Alcoholic NH_3 forms $C_6Cl_2(NH_2)_2O_2$.—7. An alcoholic solution of *aniline* reacts thus: $C_6Cl_4O_2 + 4NPhH_2 = C_6Cl_2(NPhH)_2O_2 + 2NPhH_2,HCl$ (Andresen, *J. pr.* [2] 28, 426).- 8. *m-Nitro-aniline* forms almost black crystals of $C_6Cl_4O_2(NH_2.C_6H_4.OH)_2$ (Niemeyer, *A.* 228, 322). 9. A hot aqueous solution of $NaNO_2$ converts it into nitranilic acid (Nef, *B.* 20, 2027).—10. By warming an acetic acid solution of *p*-amido-xylenol (4 pts.) with chloranil (1 pt.) there is formed a colouring matter $C_{24}H_{28}N_2O_3$. Sol. alcohol, ether, benzene, and acetone, insol. water. Dissolves in alkalis with a blue colour, in conc. H_2SO_4 with a greenish-blue. By CrO_3 it is oxidised to *p*-xyloquinone (Sutkowski, *B.* 20, 980).

Tetra-chloro-*o*-quinone $C_6Cl_4O_2$ [1:2:3:4:5:6]. [132°]. Obtained by oxidation of tetra-chloro-pyrocatechin with HNO_3, or directly by passing chlorine into a hot acetic acid solution of pyrocatechin until it assumes a deep reddish-yellow colour. Dark red crystals. V. sol. acetic acid (Zincke, *B.* 20, 1779).

p-DI-CHLORO-QUINONE-DI-CARBOXYLIC-ETHYL-ETHER $C_6Cl_2O_2(CO_2Et)_2$ [1:4:2:5:3:6]. [195°]. Formed by the action of chlorine upon quinone-di-hydro-di-carboxylic ether (di-oxy-terephthalic ether) or upon succinyl-succinic ether, suspended in alcohol. Greenish-yellow needles. Sol. acetic acid and chloroform, sl. sol. alcohol and ether. The Cl atoms are extremely mobile: thus by very dilute NaOH it is dissolved with formation of di-oxy-quinone-di-carboxylic ether; by NH_3 or amines it is readily converted into di-amido-quinone-di-carboxylic ether or its alkyl-derivatives. It is reduced by zinc-dust and acetic acid to the colourless di-chloro-hydroquinone-di-carboxylic ether (di-chloro-di-oxy-terephthalic ether, *q.v.*) (Hantzsch a. Zeckendorf, *B.* 20, 1810).

Dihydride $C_6H_2O_2Cl_2(CO_2Et)_2$. The colourless di-chloro-di-oxy-terephthalic ether becomes intense greenish-yellow when melted, changing to the tautomeric dihydride of tetra-chloro-quinone di-carboxylic ether. The colourless body dissolves in benzene, chloroform, and conc. SO_4H_2 with an intense greenish-yellow colour, whereas the solution in alcohol is colourless; the formation of an alcoholate (with 2HOEt) appears in the latter case to hinder the tautomeric change. This alcoholate can be dissociated by adding benzene to the colourless alcoholic solution when it turns yellow (Hantzsch a. Herrmann, *B.* 21, 1757).

CHLORO-QUINONE-CHLORIMIDE

$C_6H_3Cl\left\langle\begin{matrix}NCl\\ |\\ O\end{matrix}\right.$ $\left[2\,\begin{smallmatrix}4\\1\end{smallmatrix}\right]$. Formed by adding bleach ing powder to a solution of the hydro-chloride of chloro-*p*-amido-phenol at 0° (Kollrepp, *A.* 234, 16). Yellow needles (from alcohol or HOAc).

Di-chloro quinone-chlorimide $C_6H_2Cl_2\left\langle\begin{array}{l}NCl\\ |\\ O\end{array}\right.$ $\left[6:2:{}^{4}_{1}\right]$. [67°]. From di-chloro-*p*-amido-phenol hydrochloride by treatment in the cold with bleaching powder (Kollrepp, *A.* 234, 19). Yellow needles; sol. alcohol; decomposes at 170°.

Di-chloro-quinone di-chlorimide $C_6H_4\left\langle\begin{array}{l}NCl\\ |\\ NCl\end{array}\right.$. Prepared by the action of chloride of lime on an acid solution of *p*-phenylene-diamine (Krause, *B.* 12, 47). White needles. Insol. cold water, sol. hot water, alcohol ether, C_6H_6 &c. Neutral body. On reduction it gives *p*-phenylene-diamine. By boiling with HCl it gives tetrachlorophenylene diamine. Bromine in acetic acid solution converts it into di-chloro-di-bromo-quinone.

Tri-chloro-quinone chlorimide $C_6HCl_3\left\langle\begin{array}{c}O\\ NCl\end{array}\right\rangle$. [118°].

Preparation.—By stirring a slightly acid solution of tri-chloro-*p*-amido-phenol (*q. v.*) with a solution of bleaching powder (Schmitt a. Andresen, *J. pr.* [2] 23, 438; 28, 427).

Properties.—Long yellowish needles, with rough ends. V. sol. hot alcohol, ether and benzene, less sol. cold water. When melted it forms a light-brown liquid, which boils at 185° with decomposition.

Reactions.—1. *Aniline* (3 equivalents) forms di-chloro-quinone dianilide:

$$C_6Cl_3H\left\langle\begin{array}{c}O\\ NCl\end{array}\right\rangle + 3PhNH_2 + H_2O$$

$$= C_6Cl_2(NPhH)_2\left\langle\begin{array}{c}O\\ O\end{array}\right\rangle + PhNH_2,HCl + NH_4Cl.$$

But when excess of aniline (5 mols.) is added to saturated alcoholic solution of the chloro-imide at 60° a violent reaction occurs, and the crystals which ultimately separate contain another body also. This is *di-phenyl-di-amido-chloro-quinone-chloro-phenyl-imide*, $C_6Cl(NPhH)_2H\left\langle\begin{array}{c}NPh\\ O\end{array}\right\rangle$, [195°]. It forms long elastic needles (from alcohol). It is sol. ether, benzene, glacial acetic acid and CS_2. (*a*) Nitrous acid passed into its alcoholic solution produces an unstable nitroso-derivative. (*b*) It is not affected by boiling aqueous potash, but is converted by alcoholic potash into glittering red needles of $C_6Cl(NPhH)_2H(ONa)(NPhNa)$. But this compound is so unstable that alcohol reconverts it into the original body with simultaneous formation of NaOEt. (*c*) Fuming HCl mixed with alcohol reacts thus:

$$C_6Cl(NPhH)_2H\left\langle\begin{array}{c}NPh\\ O\end{array}\right\rangle + H_2O + HCl$$

$$= C_6Cl(NPhH)_2H\left\langle\begin{array}{c}O\\ O\end{array}\right\rangle + PhNH_2,HCl$$ (Andresen, *J. pr.* [2] 28, 427).—2. The ethyl derivative of *o*-amido-phenol ($C_6H_4(OEt)NH_2$) acts upon tri-chloro-quinone-chlorimide in a similar way, forming di-ethoxy-di-phenyl-di-chloro-quinone: $C_6Cl_2(NH.C_6H_4.OEt)_2O_2$. This body melts about [200°], crystallises from alcohol in glittering brown prisms, and is thrown down as a grass-green pp. when water is added to its alcoholic solution. It is not dissolved by alkalis, but forms a deep-blue solution with H_2SO_4.—3. *Di-methyl-aniline* in warm alcoholic solution acts thus: $C_6Cl_3H\left\langle\begin{array}{l}O\\ |\\ NCl\end{array}\right. + 2PhNMe_2 =$

$$C_6Cl_3H\left\langle\begin{array}{l}O\\ |\\ N.C_6H_4.NMe_2\end{array}\right. + C_6H_5NMe_2,HCl.$$

Tri-chloro-quinone-di-methyl-amido-phenyl-imide is almost insoluble in water. It crystallises from alcohol in golden-green needles which have a blue streak (when scratched) and are very tough. It is v. sol. ether, benzene, and chloroform. It is reduced by SO_2 to di-methyl-amido-phenyl-tri-chloro-phenol, $C_6Cl_3H(OH).NH.C_6H_4NMe_2$. This latter is insoluble in water, readily soluble in ether, benzene and chloroform. Recrystallised from alcohol, it melts at [139°], but its alcoholic solution is readily oxidised by the air to the preceding imide. *Salt.*—B'HCl. The *sulphonic acid* of this base $C_6Cl_3(SO_3H)(OH).NH.C_6H_4NMe_2$ is formed along with the base itself by the action of SO_2 on tri-chloro-quinone-di-methyl-amido-phenyl-imide. It crystallises in pearly plates when HCl is added to its solution in NH_3. It is insoluble in water, alcohol, ether and benzene. $BaCl_2$ added to a solution of the acid in an alkali gives a pp. which may be recrystallised from hot water (Schmitt a. Andresen, *J. pr.* 132, 426).—4. Aqueous HCl acts upon tri-chloro-quinone-chloro-imide as follows:

$$C_6Cl_3H\left\langle\begin{array}{c}NCl\\ O\end{array}\right\rangle + H_2O + 2HCl$$

$$= C_6Cl_3H\left\langle\begin{array}{c}O\\ O\end{array}\right\rangle + NH_4Cl + Cl_2.$$ HBr acts similarly (Andresen, *J. pr.* [2] 28, 435).

Di-chloro-quinone-di-chlorimide $C_6H_2Cl_2\left\langle\begin{array}{l}NCl\\ |\\ NCl\end{array}\right.$ [5:2:4:1]. [135°]. Formed by treatment of a dilute HCl solution of di-chloro-*p*-phenylene diamine [164°] with chloride of lime (Möhlau, *B.* 19, 2011). Colourless prisms (from ether). Sublimable.

CHLORO-RESORCIN $C_6H_3Cl(OH)_2$. [89°]. (256°).

Preparation.—Sulphuryl chloride (1¼ pts.) is added gradually to a solution of resorcin (1 pt.) in dry ether (3 pts.). $C_6H_4(OH)_2 + SO_2Cl_2 = HCl + SO_2 + C_6H_3Cl(OH)_2$.

Properties.—Sol. water, alcohol, ether, benzene, and CS_2. Crystallises with difficulty. Its aqueous solution is feebly acid to litmus. Ammonia turns its aqueous solution first yellow, then green; acids decolourise this liquid. Fe_2Cl_6 gives a bluish-violet colour. Ammoniacal silver solution is reduced on boiling (G. Reinhard, *J. pr.* 125, 322). *Bromine* gives chloro-di-bromo-resorcin (*q. v.*).

Benzoyl derivative $C_6H_3Cl(OBz)_2$. [98°]. Hexagonal crystals (from alcohol). Insol. water.

Di-methyl ether $C_6H_3Cl(OMe)_2$. [118°]. From di-methyl resorcin in HOAc and Cl (Hönig, *B.* 11, 1039). Long needles (from alcohol). Insol. cold HOAc, v. sol. ether.

Di-chloro-resorcin $C_6H_2Cl_2(OH)_2$. [77°]. (249°). Formed by stirring, and finally melting, a mixture of sulphuryl chloride (2½ pts.) with

resorcin (1 pt.). Purified by sublimation. The **yield is** 80 **p.c. (G.** Reinhard, *J. pr.* [2] 17, 328).

Properties.—**V.** sol. water, alcohol, ether, **benzene, and** CS_2. **Aqueous solutions are** feebly **acid to litmus,** reduce boiling **ammoniacal** silver **nitrate, and give** a bluish red **colour with** Fe_2Cl_6.

Reactions. 1. With *bromine-water* it gives di-chloro-bromo-resorcin (*q. v.*).—2. With $ClSO_3H$ **it** forms **a** crystalline insoluble **powder** $C_{12}H_6Cl_4S_2O_9$, probably the anhydride of di-chloro-resorcin sulphonic acid $(C_6HCl_2(SO_3H)OH)_2O$.

Benzoyl derivative $C_6HCl_2(OBz)_2$ [127°].

Di-methyl ether $C_6H_2Cl_2(OMe)_2$. From di-methyl-resorcin in HOAc by Cl (Honig, *B.* 11, 1039). Oil; decomposed at 110°.

Sulphonic acid $C_6HCl_2(OH)_2SO_3H$. A **white** powder, sol. water and alcohol. Formed **by** dissolving its anhydride (see above) in K_2CO_3, **acidifying,** evaporating, **and** extracting with **alcohol.** *Salt.* BaA'_2.

Tri-chloro-resorcin $C_6HCl_3(OH)_2$. [83°] and **[78°].**

Preparations.—**1.** By digesting resorcin with **sulphuryl chloride (6 pts.) for 3 hours at** 100°. **Crystallised from** water The yield is 30 p.c.—**2. Resorcin (20 g.)** dissolved in water (80 g.) **is kept cool and** treated with chlorine gas until the **red** colour, which first appears, is nearly gone. **The** liquid **is** heated **to** 70°, filtered from resin **and allowed to** deposit **crystals.** 3. By chlorinating **a** solution of resorcin (100 g.) in HOAc **(250 g.)** (Benedikt, *M.* 4, 224).

Properties. Silky needles, sl sol. cold water, **v. sol. hot water,** alcohol, **and** ether. When **purified by sublimation** it is yellow and melts at **[73°]. Its** solutions resemble those of chloro-**resorcin in** behaviour towards litmus **and** $AgNO_3$. **With** Fe_2Cl_6 it gives **a** wine-red **colour on warming** (Reinhard, *J. pr.* [2] 17, 336). **Oxidised by** K_3FeCy_6 to $C_6H_2Cl_2O_3$ [60°] (Stenhouse **a. Groves,** *B.* 13, 1307).

Benzoyl derivative $C_6HCl_3(OBz)_2$. [133°]. **Glittering** prisms (from **alcohol**).

Tri-chloro-resorcin $C_6HCl_3(OH)_2$. [69°]. **Formed by** the action of $KHSO_3$ on penta-chloro-**resorcin** (Claassen, *B.* **11, 1441).** White needles. **V. sol.** alcohol, ether, and **hot** water. **May** be **identical** with the preceding.

Tetra-chloro-resorcin. *Di-propyl ether* $C_6Cl_4(OC_3H_7)_2$. From di-propyl-resorcin and Cl **(Kariof,** *B.* 13, 1678). Liquid; decomposed at **100°.** Sol. alcohol and HOAc; sl. sol. water.

Penta-chloro-resorcin $C_6Cl_4(OH)(OCl)$ or $C_6Cl_3(Cl_2)O(OH)$. [92·5°]. Formed by adding **alternately in small** portions $KClO_3$ (5 pts.) and **a solution of** resorcin (2 pts.) in HCl (8 pts.) to **cooled** HCl (40 pts of S.G. 1·17) (Stenhouse, *Pr.* **20, 78). Plates** or flat **prisms** (from CS_2). **V. sol.** CS_2, **and** benzene, v. e. sol. alcohol **and** ether. **Changes in the air** into a modification melting **at 65° (Liebermann** a. Dittler, *A.* 169, 265). **Hot water** effects the same change.

Reactions.—1. Dissolves in a cold solution of **potassium bisulphite** with evolution **of heat** and **formation of tri-chloro**-resorcin [69°] (**Claassen,** *B.* **11, 1441). III appears also to form tri-chloro-**resorcin (Stenhouse, *C. N.* **23,** 230).—2. Unlike penta-bromo-resorcin, it is **not affected by** aldehyde and formic acid.

CHLORO-RETENE *v.* Retene.

CHLORO-ROSANILINE *v.* Di-chloro-tri-amido-tri-phenyl-carbinol.

CHLORO-SALICIN *v.* Salicin.

CHLORO-SALICYLIC ACID *v.* Chloro-*o*-oxy-benzoic acid.

CHLORO-SALICYLOL *v.* Chloro-*o*-oxy-benzoic aldehyde.

CHLORO-SALIGENIN *v.* Chloro-oxy-benzyl alcohol.

PER-CHLORO-SEBACIC ACID $C_{10}Cl_{16}H_2O_4$.

Per-chloro-butyl ether $C_{10}Cl_{16}(C_4Cl_9)_2O_4$. [172°]. (200°). From butyl sebacate and Cl in sunshine (Gehring, *C. R.* 104, 1624). **Hexagonal** prisms.

Per-chloro-isoamyl ether $C_{10}Cl_{16}(C_5Cl_{11})_2O_4$. [179°]. From isoamyl sebacate and Cl in sunshine (G.). Tough trimetric prisms (by sublimation); **volatile** with **steam.** Insol. water, **sl. sol.** alcohol, **v. sol.** ether, **benzene,** chloroform, and ligroin.

CHLORO-STEARIC ACID $C_{18}H_{35}ClO_2$. From stearic **acid and** Cl **at** 100° (Hardwick, *C. J.* **2,** 232).

CHLORO-STILBENE *v.* Chloro-di-phenyl-ethylene.

CHLORO-STRYCHNINE *v.* Strychnine.

(ω)-**CHLORO-STYRENE** $C_6H_5.CH:CHCl$. (196°) at 716 mm.

Formation.—1. By distilling styrene dichloride $C_6H_5.CHCl.CH_2Cl$ either alone or over CaO (Blyth a. Hofmann, *A.* 53, 310). 2. By heating $C_6H_5.CH_2.CHCl_2$ with **alcoholic** KOH **at** 120° (Forrer, *B.* 17, 983).

Properties. Liquid, with pungent odour. Conc. alcoholic KOH followed by distillation with water gives phenyl-acetic aldehyde. KCy gives the nitrile of phenyl-succinic acid (Rügheimer, *B.* 14, 428).

(α)-**Chloro-styrene** $C_6H_5.CCl:CH_2$. (199°). **S.G.** ^{23} **1·112.**

Formation.—1. By treating cinnamic **acid** with KOCl **or with** HCl and potassium **chlorate** (Stenhouse, *A.* 55, 1; 57, 79).—2. By heating $C_6H_5.CHCl.CH(OH)CO_2H$ with water **at** 210° (Glaser, *A.* 154, 166).—3. From $C_6H_5.CCl_2.CH_3$ and alcoholic KOH (Friedel, *C. R.* 67, 1192; Erlenmeyer, *B.* 12, 1609).—4. By **neutralising a** solution of $C_6H_5.CHCl.CHCl.CO_2H$ (**Erlenmeyer,** *B.* 14, 1867).

Properties.—**Liquid, with the odour of** hyacinths. Does **not so readily** give up its Cl as the preceding. **But by** heating **with water** acetophenone **may be formed (Erlenmeyer,** *B.* 14, 323).

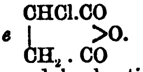
ωα-**Di-chloro-styrene** $C_6H_5.CCl:CHCl$. **(221°).** From $C_6H_5.CO.CH_2Cl$ and PCl_5 (Dyckerhoff, *B.* 10, 120, 533).

CHLORO-SUBERANE CARBOXYLIC ACID $C_7H_{12}Cl.CO_2H$. From **the** corresponding oxy-acid **and** HCl. Oil; **sol.** alcohol **and** ether. KOH gives suberene carboxylic acid $C_8H_{12}O_2$ (Dale a. Schorlemmer, *C. J.* 39, 539).

CHLORO-SUBERIC ACID $C_8H_{13}ClO_4$. From suberic acid and Cl (Bauer a. Gröger, *M.* 1, 510; 4, 341). Syrup, sol. **water,** v. e. sol. **ether.**

CHLORO-SUBERONIC ACID $C_8H_{13}ClO_2$. From oxy-suberic acid and conc. HCl at 130° (Spiegel, *A.* 211, 119). Oil; v. sol. alcohol **and ether.** Converted by sodium amalgam **into suberonic acid.** Boiling NaOHAq **forms** $C_8H_{12}O_3$.

CHLORO-SUCCINIC ACID $CO_2H.CH_2.CHCl.CO_2H$. [152°]. Prepared by heating fumaric acid with a solution of HCl in glacial acetic acid (Anschütz a. Bennert, *B.* 15, 642) Crystalline solid. Sol. water and acetic acid, sl. sol. chloroform.

Anhydride 
$\left.\begin{array}{l}\mathrm{CHCl.CO}\\ |\\ \mathrm{CH_2\,.\,CO}\end{array}\right\rangle \mathrm{O}$. [41°]. (130° at 15 mm.). Prepared by heating the acid with acetyl chloride. Formed as a by-product, when maleïc anhydride is produced by heating fumaric acid with AcCl for 8 hrs. at 140° (Perkin, *C. J.* 41, 269). Crystalline solid Sol. chloroform. On heating it decomposes into maleic anhydride and HCl.

Di-chloro-succinic acid $C_2H_2Cl_2(CO_2H)_2$. Two acids of this constitution are formed by the union of Cl with fumaric and maleic acids respectively. They differ in melting-point and solubility (Petrieff, *Bl.* [2] 41, 309).

Tetra-chloro-succinic acid. *Per-chloro-ethyl ether* $C_2Cl_4(CO_2C_2Cl_5)_2$. [116°-120°]. From succinic ether and Cl in sunshine (Cahours, *A.* 47, 294). Small needles. Decomposed by solution in alcohol, and by alcoholic KOH, tri-chloro-acetic acid being among the products. Ammonia forms tri-chloro-acetamide and other products (*cf.* Malaguti, *A. Ch.* [3] 16, 72).

CHLORO-SULPHO-ACETIC ACID $CHCl(SO_3H).CO_2H$. From chloro-acetic acid and $ClSO_3H$. Formed also by oxidation of thio-hydantoïn by $KClO_3$ and HCl (Andreasch, *M.* 7, 159).—BaA″aq: S. 2·5 at 17°.—K_2A'' 1½aq.—$(NH_4)_2A''$: needles, v. sol. water.—Ag_2A'' ½aq: prisms.

CHLORO-SULPHO-BENZOIC ACID $C_7H_5ClSO_5$ *i.e.* $C_6H_3Cl(SO_3H)(CO_2H)$ [1:3or5:2]. From *o*-chloro-toluene sulphonic acid by oxidation with chromic mixture (Hubner a. Majert, *B.* 6, 792).—KHA″aq.—BaA″ 2aq.—PbA″ 2aq.

Chloro-sulpho-benzoic acid $C_6H_3Cl(SO_3H)(CO_2H)$ [1:3?:5]. From *m*-chloro-benzoic acid and SO_3 (Otto, *A.* 123, 216). Needles (containing *x*aq); v. sol. water, alcohol, and ether. With PCl_5 it gives di-chloro-benzoic chloride.—KHA″ 1½aq.—K_2A'' 3aq.—BaA″ 2aq.—$BaH_2A''_2$ 4aq.—$CaH_2A''_2$ 3aq.—PbA″ 3aq.

Amide $C_6H_3Cl(SO_2NH_2)(CONH_2)$: crystals.

Chloro-sulpho-benzoic acid $C_6H_3Cl(SO_3H)(CO_2H)$ [1:2:4]• From *p*-chloro-benzoic acid and fuming H_2SO_4 at 130° (Collen, *A.* 191, 29; *B.* 9, 758, 1248). Long needles (from water). Sl. sol. alcohol and ether.

Salts.—NaHA″ 2aq.—Ag_2A'' aq.—BaA″ 3aq. MgA″ 6aq.—ZnA″ 4aq.—CuA″ 6aq.—PbA″ 4aq.

Chloride $C_6H_3Cl(SO_2Cl)CO_2H$. [140°-150°]. Needles (from ether).

(α)-CHLORO-TEREBIC ACID $C_7H_9ClO_4$ *i.e.* $(CH_3)_2C.CH(CO_2H).CH_2.CO.O$? (Frost, *A.* 226, 363). [191°]. From terebic acid (1 mol.) and PCl_5 (3 mols.) (Williams, *B.* 6, 1097; Roser, *A.* 220, 265). The (β)-isomeride is formed at the same time. V. sol. hot water, alcohol, or ether. At 150° it begins to sublime.

Reaction.—1. Splits off HCl, forming terebilenic acid $C_7H_8O_4$ (*q.v.*), when heated to 200°, or with water at 140°, or by boiling with NaOEt (W. Roser, *A.* 220, 261).—2. Boiled with water and $CaCO_3$ it forms oxy-terebic acid.—3. With PCl_5 at 130°-140° forms chloro-terebilenic acid.

Salts.—CaA″ 2aq.—AgHA″. PbA″ 3aq.

(β)-Chloro-terebic acid $C_7H_9ClO_4$ *i.e.* $(CH_3)_2.C.CBr(CO_2H).CH_2.CO.O$(?) [168°]. Formed by the action of Cl on teraconic acid in presence of water in the cold. Colourless, transparent, trimetric crystals; $a:b:c = 0·9827:1:0·7137$. Easily decomposed by boiling water into HCl and terebilic acid: $C_7H_8O_4$ (Frost, *A.* 226, 363).

CHLORO-TEREBILENIC ACID $C_7H_7ClO_4$ *i.e.* $Me_2C.C(CO_2H):CCl.CO.O$ (?) [200°-203°]. From chloro-terebic acid [191°] and PCl_5 at 140° (W. Roser, *A.* 220, 265). Small prisms. V. sol. water. Not affected by boiling water, hardly even by boiling with moist Ag_2O.

Salts.—CaA'_2 2aq.—AgA′.

CHLORO-TEREPHTHALIC ACID $C_6H_3Cl(CO_2H)_2$ [1:2:5]. [123°]. Formed by oxidising $C_6H_3Cl(C_2H_5)_2$ with bichromate mixture and separating the two isomeric acids formed by boiling water. White crystals; insol. boiling aq; sol. ammonia, reppd. by HCl as a curdy pp. resembling AgCl; sl. sol. warm alcohol; sol. benzene, $CHCl_3$, CS_2 and ether; sol. hot ligroïn. Sublimes at 100°. It distils without forming any anhydride (Istrati, *A. Ch.* [6] 6, 418).

Chloro-terephthalic acid $C_6H_3Cl(CO_2H)_2$ [2:1:4]. [above 300°]. Obtained by the action of cuprous chloride upon the diazo- compound from amido-terephthalic acid. Colourless crystals. V. sol. alcohol and ether, sl. sol. hot water.—Ag_2A'': white pp.

Di-methyl ether A″Me_2: [60°]; silky plates; v. sol. alcohol and ether, sl. sol. water.

Chloride $C_6H_3Cl(COCl)_2$: (c. 300°); crystalline.

Amide $C_6H_3Cl(CONH_2)_2$: [above 300°]; white crystalline crusts; sl. sol. water (Ahrens, *B.* 19, 1638).

Di-chloro-terephthalic acid $C_6H_2Cl_2(CO_2H)_2$ [5:2:4:1]. From the dihydride and dilute HNO_3. Hair-like needles; does not melt at 300°.

Methyl ether Me_2A''. [132°].

Dihydride $C_6H_4Cl_2(CO_2H)_2$. [c. 274°]. From succinyl-succinic ether (1 mol.) and PCl_5 (4 mols.) (Levy a. Andreocci, *B.* 21, 1163). Scales (from water). V. sol. alcohol and ether, sl. sol. benzene, $CHCl_3$, and CS_2.—BaA″ 3aq.—CaA″ 4aq.—NaHA″ 3aq.—Ag_2A''.—Me_2A''. [110°].—Et_2A''. [71°].

TRI-CHLORO-DI-THIENYL-ETHANE $CCl_3.CH(C_4H_3S)_2$. [76°]. Obtained by adding H_2SO_4 to a mixture of thiophene and chloral dissolved in acetic acid (Peter, *B.* 17, 1311). Colourless tables. V. sol. ether, petroleum-ether, CS_2, and hot alcohol, sl. sol. cold alcohol. Heated with isatin and H_2SO_4 it gives a violet-red colour.

DI-CHLORO-DI-THIËNYL-ETHYLENE $CCl_2:C(C_4H_3S)_2$. Formed by boiling tri-chloro-di-thiënyl-ethane with alcoholic KOH, or, better, KCN (Peter, *B.* 17, 1313). Colourless oil. Volatile with steam. With isatin and H_2SO_4 it gives a violet-blue colour.

CHLORO-THIËNYL METHYL KETONE $C_4SH_2Cl.CO.CH_3$. *Chloro-acetothiënone.* [52°].

Formed by the action of acetyl chloride upon chloro-thiophene in presence of Al_2Cl_6. Large colourless tables (from alcohol or ether). Very volatile with steam. By alkaline $KMnO_4$ it is oxidised to chloro-thiophene-carboxylic acid [140°].

Phenyl-hydrazide $C_4SH_2Cl.C(N_2HPh).CH_3$: [108°]; yellow tables; sol. hot alcohol (Gattermann a. Römer, *B.* 19, 698).

Isomeride: THIENYL CHLORO-METHYL KETONE.

CHLORO-THIO-ACETIC ACID $CH_2Cl.CS.OH$.

Ethyl ether A′Et. (167°). Prepared by heating chloro-acetic ether with P_2S_5 at 140° (Meyer, *B.* 14, 1508). Liquid.

Di-chloro-thio-acetic acid $CHCl_2.CS.OH$.

Ethyl ether A′Et. (178°). Prepared by heating di-chloro-acetic ether with P_2S_5 at 180° (Meyer, *B.* 14, 1507). Oil.

***p*-CHLORO-DI-THIO-BENZOIC ACID** $C_6H_4Cl.CS_2H$. From $C_6H_4Cl.CCl_3$ and alcoholic potassium sulphide (Engelhardt a. Latschinoff, *Z.* 1868, 459). HgA'_2: greenish-golden laminæ (from alcohol).—PbA'_2: brick-red pp.

CHLORO-THIO-CARBONYL CHLORIDE *v.* THIO-CARBONYL CHLORIDE, vol. i. p. 695. See also PER-CHLORO-METHYL MERCAPTAN.

CHLORO-THIO-CARBONYL SULPHUR-CHLORIDE $CSCl.SCl$. (140 *in vacuo*). Oil. Formed by heating $CSCl_2$ with sulphur at 130°-150°. By chlorine it is converted into per-chloro-methyl-mercaptan and sulphur chloride, as follows: $2CSCl.SCl + 3Cl_2 = 2CCl_3.SCl + S_2Cl_2$. Heated with sulphur at about 160° it yields CS_2 and S_2Cl_2 (Klason, *B.* 20, 2381).

CHLORO-THIO-FORMIC ACID $Cl.CO.S.H$.

Amyl ether $Cl.CO.S.C_5H_{11}$. (193°). S.G. $^{17.5}$ 1·078. μ_D 1·4766.

Preparation.—By saturating amyl mercaptan with $COCl_2$, and, after a few days, fractionally distilling the product (H. Schöne, *J. pr.* [2] 32, 243).

Properties.—A liquid of unpleasant odour, between that of amyl alcohol and that of mercaptan. It does not fume in the air.

Reactions.—1. Converted by NaSMe into $CO(SC_5H_{11})(SMe)$.—2. Converted by NaOEt into $CO(SC_5H_{11})(OEt)$.—3. Dry NH_3 forms $CO(SC_5H_{11})(NH_2)$.—4. With *aniline* it forms $CO(S.C_5H_{11})NPhH$ (*v.* PHENYL THIO-CARBAMIC ACID).—5. It reacts with urea forming $NH_2.CO.NH.CO.SC_5H_{11}$ (*v.* THIO-ALLOPHANIC ACID). 6 With phenyl-thio-urea it gives rise to $NPhH.CS.NH.CO.S.C_5H_{11}$ (*v.* PHENYL-DI-THIO-ALLOPHANIC ACID).—7. With diphenyl-thio-urea it forms $NPhH.CS.NPh.CO.S.C_5H_{11}$ (*v.* DI-PHENYL-DI-THIO-ALLOPHANIC ACID).

Ethyl ether $Cl.CO.SEt$. (136°). S.G. ^{12} 1·84. From $COCl_2$ and mercaptan (Salomon, *J. pr.* [2] 7, 252). Oil. Converted by NH_3 into $NH_2.CO.SEt$.

Chloro-thio-formic acid $Cl.CS.OH$.

Ethyl ether $Cl.CS.OEt$. (136°). Formed in small quantity by the action of alcohol on $CSCl_2$ (Klason, *B.* 20, 2384). Converted by NH_3 into xanthogenamide $NH_2.CS.OEt$.

Chloro-di-thio-formic ether $Cl.CS.SEt$. (100°) *in vacuo*. S.G. ^{12} 1·141. From $CSCl_2$ and EtSH. Yellow oil, smelling like garlic (K.).

CHLORO-THIOPHENE C_4H_3ClS. (130°). Obtained, together with di-chloro-thiophene, by passing chlorine into crude thiophene (Weitz, *B.* 17, 794). Strongly refractive colourless oil. Gives the indophenine reaction.

Di-chloro-thiophene $C_4H_2Cl_2S$. (170°). Obtained, together with the mono chloro-thiophene, by passing chlorine into crude thiophene (Weitz, *B.* 17, 794). Heavy oil. Gives the indophenine reaction.

Tri-chloro-thiophene C_4SHCl_3. (206° uncor.). A by-product in the preparation of tetra-chloro-thiophene (Rosenberg, *B.* 19, 650). Heavy oil. Gives the indophenine reaction.

Tetra-chloro-thiophene C_4Cl_4S. [36°]. (245°). Obtained by passing chlorine into di-bromo-thiophene (Weitz, *B.* 17, 792). Long white needles.

CHLORO-THIOPHENE-CARBOXYLIC ACID $C_4SH_2Cl(CO_2H)$. *Chloro-thiophenic acid.* [140°]. Formed by oxidation of chloro-thiényl methyl ketone with alkaline $KMnO_4$. Colourless needles (from hot water). Sublimes in spikes. Sl. sol. water (Gattermann a. Römer, *B.* 19, 694).

TETRA-CHLORO-THIOPHENE TETRA-CHLORIDE C_4Cl_8S. [215°].

Preparation.—Chlorine is passed into a solution of iodo-thiophene in $CHCl_3$. The liquid is shaken with aqueous NaOH, the chloroform evaporated, the residue extracted with alcohol and crystallised from chloroform.

Properties.—Thick prisms, resembling urea. A pungent, but not unpleasant odour. V. sol. chloroform, ether, benzene, CS_2, glacial acetic acid, and alcohol (C. Willgerodt, *J. pr.* [2] 33, 150).

TRI-CHLORO-THIOPHENE-SULPHONIC ACID $C_4SCl_3.SO_3H$. Formed by boiling the anhydride with water or alkalis.

Anhydride $(C_4SCl_3.SO_2)_2O$. Formed by the action of pyrosulphuric acid upon tri-chloro-thiophene. White glistening crystals. Sol. benzene, nearly insol. water, alcohol, and ether (Rosenberg, *B.* 19, 651).

CHLORO-THYMOHYDROQUINONE *v.* CHLORO-HYDRO-THYMOQUINONE.

TRI-CHLORO-THYMOL $C_{10}H_{11}Cl_3O$ *i.e.* $C_6Cl_3(C_3H_7)(CH_3)(OH)$. [61°]. From thymol and Cl in daylight (Lallemand, *A. Ch.* [3] 49, 148). Lemon-yellow monoclinic prisms. Decomposes at about 180°. Conc. H_2SO_4 at 100° converts it into a crystalline body [45°] (250°).

Penta-chloro-thymol $C_{10}H_9Cl_5O$. [98°]. From thymol and Cl in bright daylight (L.) Hard crystals. At 200° it splits up into propylene, HCl, and tri-chloro-cresol.

***o*-CHLORO-THYMOQUINONE** $C_6HMePrClO_2$ [1:4:2:3:6]. Formed by oxidation of the corresponding hydroquinone with Fe_2Cl_6. Yellowish mobile oil. Easily volatile with steam. V. sol. alcohol and ether (Schniter, *B.* 20, 1317).

***m*-Chloro-thymoquinone** $C_6HMePrClO_2$ [1:4:5:3:6]. Formed from *m*-bromo-thymoquinone by treatment with chlorine, the Br being replaced by Cl. Oil (Schniter, *B.* 20, 1319).

Di-chloro-thymoquinone $C_6Cl_2MePr{<}\begin{matrix}O\\O\end{matrix}$ [99°]. The ethereal extract from the product of the action of HCl on thymo-quinone-chlorimide (*q. v.*) is evaporated and distilled with steam. It crystallises in the receiver.

Properties.—Trimetric tablets (from alcohol)

Turned brown by light. Not reduced by SO_2 (Andresen, *J. pr.* [2] 23, 176).

CHLORO - THYMO - QUINONE CHLORIMIDE $C_6HClMePr<\begin{smallmatrix}O\\NCl\end{smallmatrix}$. An oil prepared by adding a solution of bleaching powder to the hydrochloride of chloro-amido-thymol, exactly as described under thymo-quinone-chlorimide.

Reactions. -Conc. HCl acts upon it exactly as it does upon thymo-quinone-chlor-imide, forming chloro-amido-thymol, chloro-thymoquinone, and di-chlorothymoquinone (*q. v.*) (Andresen, *J. pr.* 131, 187).

CHLORO-TIGLIC ACID $C_4H_6Cl.CO_2H$. [69°]. (210°). Formed by the action of alcoholic KOH upon (*a*)-di-chloro-di-methyl-succinic acid $CO_2H.CClMe.CClMe.CO_2H$, or by heating the silver-salt with water (Otto a. Beckurts, *B.* 18, 853). Formed also by treating methyl-aceto-acetic ether with PCl_5 followed by water (Rücker, *A.* 201, 54; Demarçay, *B.* 10, 1177). Glistening plates, or small needles. Sublimable and easily volatile with steam. V. sol. alcohol and ether, sl. sol. cold water. Decomposed by aqueous KOH at 150° into CO_2 and methyl ethyl ketone (Friedrich, *A.* 219, 359).—BaA'_2.—$ZnA'_2\,1\frac{1}{2}aq$. – AgA'.

Ethyl ether EtA'. (174°) (R.); (179°) (D.). Oil.

DI-CHLORO-TOLUCARBOSTYRIL *v.* DI-CHLORO-OXY-METHYL-QUINOLINE.

***o*-CHLORO-TOLUENE** C_7H_7Cl *i.e.* $C_6H_4(CH_3)Cl$ [1:2]. Mol. w. 126½. (154° uncor.).

Formation.—1. In small quantity, together with the *p*-modification, by chlorinating toluene in presence of iodine (Hubner a. Majert, *B.* 6, 790). 2. By running a solution of $NaNO_2$ into a hot solution of *o*-toluidine, and Cu_2Cl_2 in dilute HCl (Sandmeyer, *B.* 17, 2651; *cf.* Beilstein a. Kuhlberg, *A.* 156, 79).—3. By heating *o*-diazotoluene with a large excess of strong HCl; the yield is 40 p.c. of the theoretical (Gasiorowski a. Waÿss, *B.* 18, 1939). 4. By decomposing with superheated steam the sulphonic acid obtained by acting on commercial mono-chloro-toluene with sulphuric acid. The *o*- compound is much more easily sulphonated than the *p*- compound, and the Ca and Na salts of the resulting acid are much less soluble. The separation is, however, not a perfect one (Seelig, *A.* 237, 151, 155).

Properties.—Liquid. Converted by oxidation into *o*-chloro-benzoic acid (Wroblewsky, *Z.* [2] 5, 460). On nitration it gives a mixture of $C_6H_4(CH_3)Cl(NO_2)$ [1:2:5] and [1:2:6] (Hönig, *B.* 20, 2417).

***m*-Chloro-toluene** $C_6H_4(CH_3)Cl$ [1:3]. (156°). From *m*-toluidine by displacement of NH_2 by Cl through the diazo- reaction. Formed also by eliminating NH_2 from chloro-*p*-toluidine (Wroblewsky, *A.* 168, 199). Oxidised by CrO_3 to *m*-chloro-benzoic acid.

***p*-Chloro-toluene** $C_6H_4(CH_3)Cl$ [1:4]. [6·5°]. (160°). S.V. 134·91 (R. Schiff, *A.* 220, 99). S.G. ^{14} 1·080.

Formation.—1. By chlorinating toluene in presence of iodine, $MoCl_5$, or other carriers (Deville, *A. Ch.* [3] 3, 178; Beilstein a. Geitner, *A.* 139, 331; *Bl.* [2] 1, 251; Aronheim a. Dietrich, *B.* 8, 1402).—2. By running a solution of $NaNO_2$ into a hot solution of *p*-toluidine and Cu_2Cl_2 in dilute HCl (Sandmeyer, *B.* 17, 2651; *cf.* Hubner a. Majert, *B.* 6, 794). 3. By heating *p*-diazo toluene with a large excess of HCl; the yield is 40 p.c. of the theoretical (Gasiorowski a. Waÿss, *B.* 18, 1939).

Properties.—Liquid. Not attacked by water at 200°, nor by alcoholic NH_3 at 100° or alcoholic Na_2S, NaHS, or NaOEt at 150°. Chromic mixture gives *p*-chloro-benzoic acid. On nitration it gives (4:2:1) chloro-nitro-toluene [38°], and (4:3:1) chloro-nitro-toluene [9°] (Goldschmidt a. Hönig, *B.* 19, 2438).

ω-chloro-toluene *v.* BENZYL CHLORIDE.

(β)-Di-chloro-toluene $C_6H_3(CH_3)Cl_2$[1:2:4]. (197°) (S.). S.G. $\frac{20}{20}$ 1·2460 (L. a. K.). From $C_6H_3MeCl(NO_2)$[1:2:4] *viâ* $C_6H_3MeCl(NH_2)$ (Lellmann a. Klotz, *A.* 231, 314). Formed also by chlorinating *p*-chloro-toluene (Seelig, *A.* 237, 167) Oil. Gives di-chloro-benzoic acid [158°].

Di-chloro-toluene $C_6H_3(CH_3)Cl_2$[1:2:5]. [5°] (191° uncor.) at 745 mm. S.G. $\frac{20}{20}$ 1·2535. From $C_6H_3Me(NH_2)Cl$[1:2:5] by diazo- reaction (Lellmann a. Klotz, *A.* 231, 318). Gives di-chloro-benzoic acid [156°].

Di-chloro-toluene $C_6H_3(CH_3)Cl_2$[1:3:5]. [26°]. (195° uncor.) at 729 mm. Prepared from $C_6H_2Me(NH_2)Cl_2$[1:4:3:5] by diazo- reaction (Lellmann a. Klotz, *A.* 231, 323). Gives di-chloro-benzoic acid [182°].

(a)-Di-chloro-toluene $C_6H_3(CH_3)Cl_2$[1:2:3]. (197°). Formed by the action of chlorine on toluene in presence of ferric chloride or other carriers (Seelig, *A.* 237, 157). Yields a nitro-derivative [51°] or a dinitro- derivative [122°]. On oxidation with alkaline permanganate it gives di-chloro-benzoic acid [166°].

Di-chloro-toluene $C_6H_3(CH_3)Cl_2$ [1:3:4]. (200° uncor.) at 740 mm. S.G. $\frac{20}{20}$ 1·2512.

Formation. 1. From $C_6H_3MeCl(NH_2)$ [1:3:4] by diazo- reaction (Lellmann a. Klotz, *A.* 231, 311). 2. A product of the chlorination of toluene in presence of carriers (Beilstein a. Geitner, *A.* 139, 341; Beilstein a. Kuhlberg, *A.* 150, 313; Aronheim a. Dietrich, *B.* 8, 1401; Neuhof, *Z.* [2] 2, 653; Schultz, *A.* 187, 263). –3. From chloro-*p*-cresol and PCl_5 (Schall a. Dralle, *B.* 17, 2535).

Properties.—Oil. Gives on oxidation di-chloro-benzoic acid [201°].

ω*p*-Di-chloro-toluene [4:1] $C_6H_4Cl.CH_2Cl$. *p-Chloro-benzyl chloride.* [29°]. (213°).

Formation.—1. By chlorinating *p*-chloro-toluene at 160° (Neuhof, *A.* 146, 320; Jackson a. Field, *Am.* 2, 85; *P. Am. A.* 14, 54; *B.* 11, 904). 2. By chlorinating cold benzyl chloride in presence of iodine (N.)

Properties.—Needles or prisms; insol. water, sol. alcohol and ether. Powerfully attacks the mucous membrane. Very volatile. Oxidation gives *p*-chloro-benzoic acid. Boiling water forms *p*-chloro-benzyl alcohol. Boiling aqueous $Pb(NO_3)_2$ gives *p*-chloro-benzoic aldehyde. Alcoholic KCy forms phenyl-acetonitrile.

ωω - Di - chloro - toluene *v.* BENZYLIDENE CHLORIDE.

(a)-Tri-chloro-toluene $C_6H_2(CH_3)Cl_3$ [1:2:4:5]. [82°]. (230°). Is formed, together with the (β)-derivative, by passing chlorine into toluene in presence of Fe_2Cl_6 or other carriers (Limpricht, *A.* 139, 303; Aronheim a. Dietrich, *B.* 8, 1401; Schultz, *A.* 187, 274; Seelig, *A.* 237, 133). Long needles, sol. alcohol. Forms a sulphonic acid, which is decomposed by superheated steam at

160°. Chromic mixture oxidises it to tri-chloro-benzoic acid [163°] (Janasch, *A.* 142, 301).

(β)-Tri-chloro-toluene $C_6H_2(CH_3)Cl_3$ [1:2:3:4]. [41°]. (232°). Is formed together with the (*a*) isomeride by passing chlorine into toluene in presence of Fe_2Cl_6 (Seelig, *A.* 237, 133). Forms a sulphonate, which is decomposed by superheated steam at about 210°. Gives tri-chloro-benzoic acid [129°].

ω-*exo*-Tri-chloro toluene $C_6H_3Cl_2.CH_2Cl$. (240°). S.G. 1·44. A product of the chlorination of toluene and of benzyl chloride (Naquet, *A. Suppl.* 2, 248; Kekulé, *K.* 2, 561). Formed also by chlorinating boiling di-chloro-toluene (Beilstein a. Kuhlberg, *A.* 146, 317). Liquid. Alcoholic KOAc gives $C_6H_3Cl_2.CH_2OAc$.

ωω*o*-Tri-chloro-toluene [2:1] $C_6H_4Cl.CHCl_2$. *o-Chloro benzylidene chloride.* (c. 230°). From salicylic aldehyde and PCl_5 (Henry, *B.* 2, 135; *Z.* [2] 5, 371). Formed also, together with the following, by chlorinating benzylidene chloride in presence of iodine (B. a. K.). Water at 170° converts it into chloro-benzoic aldehyde. Chromic mixture forms *o*-chloro-benzoic acid. Distillation with dry oxalic acid forms *o*-chloro-benzoic aldehyde (Anschutz, *A.* 226, 19).

ωω*p*-Tri-chloro-toluene [4:1] $C_6H_4Cl.CHCl_2$. *p-Chloro-benzylidene chloride.* (234°). Formed as above (B. a. K.). Resembles the preceding in its reactions.

ωωω-Tri-chloro-toluene *v.* BENZOTRICHLORIDE.

Tetra-chloro-toluene $C_6HCl_4.CH_3$. [96°] (L.); [91°] (B. a. K.). (276° cor.). Among the products of chlorinating toluene in presence of $SbCl_5$ (Limpricht, *A.* 139, 327). Slender needles (from alcohol).

Tetra-chloro-toluene $C_7H_4Cl_4$. (280°-290°). From di-chloro-toluene tetrachloride and alcoholic KOH (Pieper, *A.* 142, 305).

Tetra-chloro-toluene $C_6H_2Cl_3.CH_2Cl$. *Tri-chloro-benzyl chloride.* (273°). S.G. ^{22} 1·547. From $C_6H_2Cl_3.CH_3$ and Cl at high temperatures (Beilstein a. Kuhlberg, *A.* 150, 286).

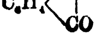
Tetra-chloro-toluene $C_6H_3Cl_2.CHCl_2$ [4:3:1]. (*a*)-*Di-chloro-benzylidene chloride.* (257°). S.G. ^{22} 1·518. From Cl and boiling (1,3,1)-di-chloro-toluene (B. a. K.). Water at 220° gives di-chloro-benzoic aldehyde.

Tetra-chloro-toluene $C_6H_3Cl_2.CHCl_2$ [1·3.6]. (β)-*Di-chloro-benzylidene chloride.* (c. 260°) Formed by passing chlorine into (β)-di-chloro-toluene heated at 230° (Seelig, *A.* 237, 167). Is converted into dichlorobenzoic aldehyde on treating with conc. H_2SO_4.

Tetra-chloro toluene [2:1] $C_6H_4Cl.CCl_3$. *o-Chloro-benzotrichloride.* [30°]. (260°) From *o*-oxy-benzoic acid by distilling with PCl_5 (Kolbe a. Lautemann, *A.* 115, 195). Water at 150° gives *o*-chloro-benzoic acid.

Tetra-chloro-toluene [3:1] $C_6H_4Cl.CCl_3$. *m-Chloro-benzotrichloride.* (235°). From *m*-sulpho-benzoic acid and PCl_5 (Carius a. Kämmerer, *A.* 131, 158).

Tetra-chloro-toluene [4:1] $C_6H_4Cl.CCl_3$. *p-Chloro-benzotrichloride.* (245°).

Formation.—1. From benzotrichloride and Cl in presence of carriers (Beilstein a. Kuhlberg, *A.* 146, 317).—2. From benzoyl chloride and PCl_5 (Limpricht, *A.* 134, 57). 3. From *p*-oxy-benzide  $C_6H_4{<}\begin{matrix}O\\|\\CO\end{matrix}$ and PCl_5. The product is freed from $POCl_3$ by distillation, and the residue shaken with dilute NaOH (Klepl, *J. pr.* [2] 28, 204).

Properties.—Oil. Converted by warm conc. H_2SO_4 or by water at 200° into *p*-chloro-benzoic acid.

Penta-chloro-toluene $C_6Cl_5.CH_3$. [218°]. (301°). Formed by chlorinating toluene in presence of iodine (B. a. K.). Needles (from benzene).

Penta-chloro-toluene $C_6HCl_4.CH_2Cl$. *Tetra-chloro-benzyl chloride* (296°). S.G. ^{22} 1·634. From boiling tetra-chloro-toluene and Cl (B. a. K.) Further chlorination gives C_6Cl_6 and CCl_4 (Beilstein a. Kuhlberg, *Z.* [2] 5, 527).

Penta-chloro-toluene $C_6H_2Cl_3.CHCl_2$ [2:4:5:1]. (*a*)-*Tri-chloro-benzylidene chloride.* (281°). S.G. ^{24} 1·607. From Cl and boiling tri-chloro-toluene (B. a. K.). Needles (below 0°). Water at 250° or cold fuming H_2SO_4 gives tri-chloro-benzoic aldehyde.

Penta-chloro toluene $C_6H_2Cl_3.CHCl_2$ [4:3:2:1]. (β)-*Tri-chloro-benzylidene chloride.* [84°]. (c. 280°). Formed by passing chlorine through boiling (β)-tri-chloro toluene (Seelig, *A.* 237, 146). Oil solidifying to a crystalline mass. Sol. petroleum ether. Treated with fuming sulphuric acid it forms (β)-tri-chloro-benzoic aldehyde.

Penta-chloro-toluene $C_6H_3Cl_2.CCl_3$. *Di-chloro-benzotrichloride.* (273°). S.G. ^{21} 1·587. From crude di-chloro-toluene and Cl (B. a. K.). Water at 200° gives a mixture of di-chloro-benzoic acids.

Hexa chloro toluene $C_7H_2Cl_6$ *i.e.* $C_6Cl_5.CH_2Cl$. *Penta-chloro-benzyl chloride.* [103°]. (326°). From benzyl chloride and Cl in presence of $SbCl_5$. Formed also by chlorinating boiling penta-chloro-toluene (B. a. K.; *cf.* Deville, *A.* 44, 304). Slender needles; sl. sol. alcohol; v. sol. benzene. Alcoholic KOAc at 200° gives $C_6Cl_5.CH_2OH$.

Hexa-chloro-toluene $C_6HCl_4.CHCl_2$. *Tetra-chloro-benzylidene chloride.* (306°). S.G. ^{25} 1·704. From Cl and boiling tetra-chloro-toluene $C_6HCl_4.CH_3$ (B. a. K.). Water at 280° gives tetra-chloro benzoic aldehyde.

Hexa-chloro-toluene $C_6HCl_3.CCl_3$. *Tri-chloro-benzotrichloride.* [82°]. (308°). From Cl and boiling $C_6HCl_3.CH_3$ (Beilstein a. Kuhlberg, *A.* 150, 305). Slender needles (from alcohol). Water at 260° gives tri-chloro-benzoic acid.

Hepta-chloro-toluene $C_6Cl_5.CHCl_2$. *Penta-chloro-benzylidene chloride.* [110°]. (334°). Formed by chlorinating benzylidene chloride with the aid of carriers (B. a. K.). Flat laminæ (from alcohol). Sl. sol. cold alcohol, v. sol. boiling alcohol. Water at 300° does not act upon it.

Hepta-chloro-toluene $C_6HCl_4.CCl_3$. [104°]. (316°). From Cl and boiling $C_6HCl_4.CH_3$ (B. a. K.). Short needles (from alcohol); m. sol. hot alcohol. Water at 270° gives tetra-chloro-benzoic acid.

CHLORO - TOLUENE - AZOXY - CHLORO - TOLUENE *v.* AZOXY- COMPOUNDS.

DI-CHLORO-TOLUENE TETRACHLORIDE $C_7H_6Cl_6$ *i.e.* $C_6H_3Cl_6.CH_3$. [150°]. From toluene and Cl (Pieper, *A.* 142, 304). Prisms (from CS_2). Alcoholic NaOH at 110° gives di-chloro-benzoic acid [203°] and tetra-chloro-toluene (c. 285°).

***p*-CHLORO-TOLUENE-(β)-SULPHONIC ACID** $C_6H_3MeCl(SO_3H)$ [1:4:2]. From *p*-chloro-toluene and H_2SO_4 (Vogt a. Henninger, *A.* 165, 362). Also from the corresponding *p*-toluidine *o*-sulphonic acid by displacement of NH_2 by Cl (Jenssen, *A.* 172, 239).

Salts.—$BaA'_2\,1\tfrac{1}{2}aq$: S. 1·9 at 16°.—$BaA'_2\,aq$ (Hubner a. Majert, *B.* 6, 790). — $KA'\,aq$. — $CaA'_2\,6aq$.—$PbA'_2\,8aq$.—$CuA'_2\,7aq$.

Amide $C_6H_3Cl.Me.SO_2NH_2$ [138°]. From $C_6H_3(NH_2)Me.SO_2NH_2$ by HCl and nitrous acid gas (Heffter, *A.* 221, 209).

***p*-Chloro-toluene (*a*)-sulphonic acid** $C_6H_3MeCl(SO_3H)$ [1:4:3]. Formed, together with the preceding, by sulphonating *p*-chloro-toluene (Vogt a. Henninger, *A. Ch.* [4] 27, 129). Converted by potash-fusion into orcin.

Salts. — $KA'\,\tfrac{1}{2}aq$: laminæ. — $NaA'\,5aq$. - $BaA'_2\,2aq$: S. 5·71 at 16·5° (V. a. H.).—$BaA'_2\,\tfrac{1}{2}aq$: S. 14 at 14·5° (Hübner a. Majert, *B.* 6, 790).—$BaA'_2\,aq$ (V. a. H.). —$BaA'_2\,7aq$ (Engelbrecht, *B.* 7, 796).—$CdA'_2\,2aq$.—$PbA'_2\,6aq$.—$CuA'_2\,10aq$.

***o*-Chloro-toluene sulphonic acid** $C_6H_3MeCl(SO_3H)$ [1:2:3or5]. From *o*-chloro-toluene and H_2SO_4 (Hubner a. Majert, *B.* 6, 790). Sodium amalgam gives toluene *m*-sulphonic acid. Oxidation forms chloro-sulpho-benzoic acid.—$NH_4A'\,aq$. — $KA'\,\tfrac{1}{2}aq$.—$NaA'\,\tfrac{1}{2}aq$. —$BaA'_2\,2aq$.—$CaA'_2\,2aq$. -$PbA'_2\,2aq$.—$CuA'_2\,\tfrac{1}{2}aq$.

Chloro-toluene sulphonic acid $C_6H_3MeCl(SO_3H)$ [1:2:4]. From the amide and HCl at 150°. Salts. —BaA'_2.— KA'.

Chloride $C_6H_3ClMe.SO_2Cl$. Oil.

Amide $C_6H_3MeCl.SO_2NH_2$. [135°]. From $C_6H_3Me(SO_2NH_2).N_2.NH.C_6H_3Me.SO_2NH_2$ and HCl (Paysan, *A.* 221, 212).

***p*-Chloro-toluene *ω*-sulphonic acid** [4:1]$C_6H_4Cl.CH_2.SO_3H$. *Chlorobenzyl sulphonic acid.* [108°] (?). From $C_6H_4Cl.CH_2Cl$ and aqueous K_2SO_3 (Böhler, *A.* 154, 56; Vogt a. Henninger, *A. Ch.* [4] 27, 129; Jackson a. White, *Am.* 2, 159; *P. Am. A.* 14, 312; *B.* 13, 1217). Potash-fusion gives *p*-oxy-benzoic acid.

Salts. —KA' (B.; J. a. W.) $KA'\,aq$ (V. a. H.): sol. boiling alcohol.—NaA': flat crystals (from water) or pearly scales (from alcohol).—$BaA'_2\,aq$.—$BaA'_2\,2aq$ (J. a. W.): Needles. -$CaA'_2\,2aq$. —$CaA'_2\,7aq$ (J. a. W.); trimetric crystals.—$CuA'_2\,2aq$: pale green needles.—$PbA'_2\,aq$ (J. a. W.): long needles. — $A'PbOH\,aq$. — $A'_2Pb_3O_2$: Needles.

Chloride $C_6H_4Cl.CH_2.SO_2Cl$. [85·5°]: flat crystals, v. sol. ether.

CHLORO-*o*-TOLUIC ACID $C_6H_3(CH_3)Cl.CO_2H$ [2:4:1]. [130°]. Formed, together with the [6:3:1] isomeride [166°], by oxidation of chloro-*o*-xylene $C_6H_3(CH_3)_2Cl$ [1:2:4] with HNO_3 (Krüger, *B.* 18, 1757). Fine needles or thick prisms. By further oxidation by means of $KMnO_4$ both acids yield chloro-phthalic acid [130°–134°]. By KOH fusion it is converted into oxy-*o*-toluic acid $C_6H_3(CH_3)(OH)CO_2H$ [2:4:1].- $CaA'_2\,3aq$.

Chloro-*p*-toluic acid $C_6H_3(CH_3)Cl(CO_2H)$ [4:2:1]. [150°]. Formed by the action of boiling dilute HNO_3 on chloro-cymene (derived from thymol and PCl_5). Slightly volatile with steam. (Fileti a. Crosa, *G.* 16, 290).

Chloro-*o*-toluic acid $C_6H_3(CH_3)Cl.CO_2H$[2:3:1]. [154°]. Formed by oxidation of chloro-*o*-xylene $C_6H_3(CH_3)_2Cl$ [1:2:3] by HNO_3 (Krüger, *B.* 18, 1758). Needles. V. sol. alcohol. By further oxidation by means of $KMnO_4$ it yields chloro-phthalic acid [181°].—$A'_2Ca\,2aq$: sparingly soluble long prisms.

Chloro-*o*-toluic acid $C_6H_3(CH_3)Cl.CO_2H$[6:3:1]. [166°]. Formed, together with the isomeride (2:4:1), by oxidation of chloro-*o*-xylene $C_6H_3(CH_3)_2Cl$ [1:2:4], with HNO_3 (Krüger, *B.* 18, 1757). Needles. Sol. alcohol, v. sl. sol. water. By further oxidation by means of $KMnO_4$ both acids yield chloro-phthalic acid [130°-134°]. By KOH fusion it yields oxy-*o*-toluic acid [173°]. —$A'_2Ca\,2aq$: sparingly soluble short prisms.

Chloro-*p*-toluic acid $C_6H_3(CH_3)Cl(CO_2H)$ [4·3:1]. [196°]. Formed by the action of boiling dilute HNO_3 on the chloro cymene that is obtained from carvacrol and PCl_5 (Fleischer a. Kekulé, *B.* 6, 1090; v. Gerichten, *B.* 10, 1249; 11, 366). Laminæ.—$CaA'_2\,3aq$. $BaA'_2\,4aq$.

Chloro-*m*-toluic acid $C_6H_3(CH_3)Cl.CO_2H$ [3:4:1]. [203°] (V.); [210° cor.] (J.); [204° cor.] (R. a. K.).

Formation.—1. By oxidation of chloro-*m*-xylene $C_6H_3(CH_3)_2Cl$ [1:3:4] with $K_2Cr_2O_7$ and H_2SO_4 (Vollrath, *Bl.* [2] 7, 342; Jacobsen, *B.* 18, 1761).—2. From $C_6H_3(CH_3)(NO_2)(CO_2H)$ [3:4:1] by displacement of NO_2 by Cl (Beilstein a. Kreusler, *A.* 144, 182; Remsen a. Kuhara, *Am.* 3, 431).

Properties.—Needles (from alcohol). By KOH fusion it gives oxy-*m*-toluic acid [173°].

Salts. -$BaA'_2\,3aq$: slender needles (V.).—$CaA'_2\,3aq$.

Ethyl ether EtA'. (263°).

***ω*-Chloro-*o*-toluic acid** *Amide* [2:1] $CH_2Cl.C_6H_4.CONH_2$. [c. 180°]. From the nitrile and H_2SO_4 at 90°, followed by water (Gabriel, *B* 20, 2234). Slender needles (from alcohol). Boiling water converts it into phthalide. At 160 it changes to oily 'pseudophthalimidine' C_8H_7NO.

Nitrile $CH_2Cl.C_6H_4.CN$. *o-Cyano-benzyl chloride.* [61°]. (252°). Formed by passing Cl into the boiling nitrile of *o*-toluic acid (Gabriel a. Otto, *B.* 20, 2223). Monoclinic crystals; *a*:*b*:*c* - ·778:1: ·291; $\beta = 60°\,2'$. Sol hot water.

Di-chloro-toluic acid $C_6H_2(CH_3)Cl_2(CO_2H)$. [161°]. From crude di-chloro-xylene (222°) and chromic mixture (Hollemann, *A.* 144, 269).—$CaA'_2\,9aq$. -AgA'.

Di-*ω*-chloro-toluic acid. *Nitrile* $CHCl_2.C_6H_4.CN$. *Cyano-benzylidene chloride.* (260°). Formed by the action of chlorine on the boiling nitrile of *o*-toluic acid (Gabriel a. Weise, *B.* 20, 3197). Fuming HCl at 170° gives $C_6H_4(CHO)(CO_2H)$. [97°].

Tri-*ω*-chloro-*o*-toluic acid. *Nitrile* $CCl_3.C_6H_4.CN$. *Cyano-benzyl trichloride.* [95°]. (c. 280°). From boiling *o*-toluic nitrile and Cl (G. a. W.). Monoclinic crystals (from alcohol); *a*:*b*:*c* = 1·546:1:1·106; $\beta = 73°\,53'$.

***o*-CHLORO-*o*-TOLUIDINE** $C_6H_3(CH_3)Cl(NH_2)$ [1:2:6]. Formed by reduction of the corresponding nitro- compound (the nitration-product of *o*-chloro-toluene). Liquid.

Acetyl derivative $C_7H_6Cl.NHAc$: [136°]; white needles (Hönig, *B.* 20, 2417)

***s*-Chloro-toluidine** $C_6H_3(CH_3)Cl(NH_2)$ [1:3:5]. (242°) at 730 mm. Formed by reduction of the corresponding nitro- compound. Liquid. Volatile with steam.—$B'HNO_3$: [198°], colourless needles

Acetyl derivative $C_7H_6Cl(NHAc)$: [198°]; colourless needles (Honig, *B* 20, 2419).

Chloro-*p*-toluidine $C_6H_3(CH_3)Cl(NH_2)$ [1:3:4]. [7°]. (219° uncor.). Got by boiling its acetyl derivative with HCl. Elimination of NH_2 gives *m*-chloro-toluene. –B'HCl. –$B'HNO_3$. S. 2·59 at 19°. –$B'H_2SO_4$.—$B'H_2C_2O_4$.

Acetyl derivative $C_6H_3MeCl(NHAc)$ [1:3:4]. [115°]. Formed by chlorination of *p*-acet-toluide. Bad yield (Lellmann a. Klotz, *A.* 231, 309; *cf* Wroblewsky, *A* 168, 196).

***p*-Chloro-*o*-toluidine** $C_6H_3(CH_3)Cl(NH_2)$ [1:4:2]. [22°]. (237 at 722 mm.). Colourless liquid or white crystalline solid. Formed by reduction of (4:2:1)-chloro-nitro-toluene [38°].

Salts.—B'HCl: colourless needles. — $B'_2H_2Cl_2PtCl_4$ 2aq: fine yellow needles.

Acetyl derivative $C_6H_3(CH_3)Cl.NHAc$: [131°]; long slender colourless needles, v. sol. hot water, alcohol and ether, sl. sol. cold water (Goldschmidt a. Hönig, *B* 19, 2440; *cf.* Engelbrecht, *B.* 7, 797; and Beilstein a. Kuhlberg, *A.* 158, 336).

Chloro-*p*-toluidine $C_6H_3(CH_3)(Cl)(NH_2)$ [1:2:4]. [26°]. (238°). Formed by reduction of chloro-nitro-toluene [65°] (Lellmann, *B.* 17, 585). Colourless crystalline solid V. sol. all solvents except water. By diazotisation and treatment with alcohol it yields *o*-chloro-toluene.

Salts.– B'HCl: broad colourless needles.— $B'_2H_2SO_4$: small colourless plates. –$B'_2H_2PtCl_6$.

Acetyl derivative $C_6H_3MeCl(NHAc)$. [105°]. From $C_6H_3Me(NHAc).N_2\,NC_5H_{10}$ and boiling HClAq (Wallach, *A.* 235, 254).

***p*-Chloro-*m*-toluidine** $C_6H_3(CH_3)Cl(NH_2)$ [1:4:3]. [28°] (G. a. H.); [30°] (G. a. K.). (230°). Formed by reduction of (4:3:1)-chloro-nitro-toluene [9°]. White crystalline solid. The base and its salts are extremely soluble. - B'HCl: colourless tables.

Acetyl derivative $C_6H_3(CH_3)Cl.NHAc$: [97°]; long silky needles, m. sol. water (Goldschmidt a. Honig, *B.* 19, 2442; *cf.* Engelbrecht, *B.* 7, 797; and Gattermann a. Kaiser, *B.* 18, 2599).

Chloro-*o*-toluidine $C_6H_3(CH_3)Cl(NH_2)$ [1:5:2]. [30°]. (237° uncor.) at 730 mm. From its acetyl derivative (L. a. K.). The same compound ([30°], (241°)) appears to be a by-product in the reduction of *o*-nitro-toluene by tin and HCl (Beilstein a. Kuhlberg, *A.* 156, 81).

Salt.—B'HCl: sl. sol. water.

Acetyl derivative $C_6H_3Me(NHAc)Cl$. [140°]. Got by chlorination of acetylated *o*-toluidine (Lellmann a. Klotz, *A.* 231, 317).

***o*-Chloro-*m*-toluidine** $C_6H_3MeCl(NH_2)$ [1:2:5]. [83°]. (239°) at 215 mm. Obtained by reduction of the corresponding nitro- compound [44°] (Goldschmidt a. Hönig, *B.* 19, 2443; 20, 199; Wroblewsky, *A.* 168, 200; Henry a. Radziszewsky, *B.* 2, 308, 599). Formed also as a by-product in the reduction of *m*-nitro-toluene by zinc-dust and HCl (Kock, *B.* 20, 1567). Glistening colourless needles of characteristic odour.

Salts.—B'HCl: long slender needles.— $B'HNO_3$: [164°], broad colourless needles. S. 5·01 (W.).—$B'_2H_2SO_4$.

Acetyl derivative $C_6H_3MeCl(NHAc)$: [89°]; colourless plates.

Di-chloro-*p*-toluidine $C_6H_2(CH_3)Cl_2(NH_2)$ [1:3:5:4]. [60°]. Needles (from dilute alcohol). V. sol. alcohol and ether. Weak base. May be sublimed.

Acetyl derivative $C_6H_2Me(NHAc)Cl_2$ [1:4:3:5]. [201°]. From $C_6H_3Me(NHAc)Cl$ [1:4:3] by chlorination (Lellmann a. Klotz, *A.* 231, 322). White needles (from alcohol). V. sol. alcohol, insol. water, sol. ether and glacial acetic acid. May be sublimed.

(β)-Di-chloro-toluidine $C_6H_2(CH_3)Cl_2(NH_2)$. [1:2:4:?]. [87°]. (259°). Formed by reducing (β)-di-chloro-nitro-toluene [53°] (Seelig, *A.* 237, 163). Plates (from methyl alcohol).

Di-chloro-toluidine $C_6H_2(CH_3)Cl_2(NH_2)$ [1:2:4:6]. [88°]. (259°). Obtained by reducing di-chloro-nitro-toluene [-14°] (Wroblewsky, *A.* 168, 213). Does not combine with acids.

Tri-chloro-toluidine $C_6H(CH_3)Cl_3(NH_2)$ [1:2:4:6:3] or [1:2:4:5:6]. [91°] (Schultz, *A.* 187, 278); [95°] (Seelig, *B.* 18, 423). From tri-chloro-nitro-toluene [89°], tin and HCl. Needles (from alcohol).

Acetyl derivative $C_6H(CH_3)Cl_3(NHAc)$. [191°].

Benzoyl derivative $C_6H(CH_3)Cl_3(NHBz)$. [213°].

Tri-chloro-toluidine $C_6H(CH_3)Cl_3(NH_2)$ [105°]. From (β)-tri-chloro-nitro-toluene, $SnCl_2$, and HCl (Seelig, *B.* 18, 423) Needles.

CHLORO-TOLUQUINOLINE *v.* CHLORO-(*B.*)-METHYL-QUINOLINE.

CHLORO-TOLUQUINONE $C_6H_2(CH_3)ClO_2$. [1:4or3:2:5]. [90° uncor.]. Formed by oxidation of di-chloro-*o*-cresol with $K_2Cr_2O_7$ and dilute H_2SO_4. Long yellow needles. Volatile with steam, and sublimable. V. sol. alcohol, ether, &c., sol. hot water, sl. sol. cold. Dissolves in alkalis with a dark-red colour. By SO_2 it is reduced to chloro-hydrotoluquinone [115°] (Claus a Sweitzer, *B.* 19, 929).

Chloro-toluquinone $C_6H_2(CH_3)ClO_2$. [105°]. From chloro-hydro-toluquinone [175°] by distillation with aqueous Fe_2Cl_6 (Schniter, *B.* 20, 2282).

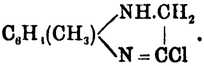
Di-chloro-toluquinone $C_6H(CH_3)Cl_2O_2$ [1:2:4:3:6]. [103° uncor.]. Glistening yellow plates. Volatile with steam. Formed by oxidation of di-chloro-*m*-cresol with $K_2Cr_2O_7$ and H_2SO_4. Also from *m*-cresol, HCl, and $KClO_3$ (Southworth, *A.* 168, 270). Yellow tables (from alcohol). The corresponding di-chloro-hydro-toluquinone melts at [171°] (Claus a. Schweitzer, *B.* 19, 931).

Di-chloro-toluquinone $C_6H(CH_3)Cl_2O_2$ [1:?:?:2:5]. From *o*-cresol, $KClO_3$, and HCl (Southworth, *A.* 168, 274). Not obtained pure. Reduced by SO_2 to di-chloro-hydrotoluquinone [121°].

Tri-chloro-toluquinone $C_6(CH_3)Cl_3O_2$. [232°]. From *o*-cresol, HCl, and $KClO_3$ (Græbe a. Borgmann, *A.* 152, 248; Southworth, *A.* 168, 273; Knapp a. Schultz, *A.* 210, 176). Formed also by treating *o*-toluidine sulphonic acid with $KClO_3$ and HCl (Hayduck, *A.* 172, 209). Yellow plates; sl. sol. cold alcohol, v. sol. ether. Volatile with steam.

Tetra-chloro-toluquinone $CH_2Cl.C_6Cl_3O_2$. Occurs among the products of the action of HCl and $KClO_3$ on beech-wood creosote (Gorup-Besanez, *A.* 143, 159; Bräuninger, *A.* 185, 339). Golden scales. May be sublimed. Sl. sol. cold alcohol.

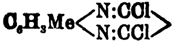
CHLORO-TOLUQUINOXALINE *Dihydride.*



$C_9H_9N_2Cl$ *i.e.* $C_6H_3(CH_3)<\begin{matrix}NH.CH_2\\ |\\ N=CCl\end{matrix}$. [77°].

Formed by heating oxy-di-hydro-toluquinoxaline with PCl_5. Long colourless needles. Insol. water, v. e. sol. other solvents. Volatile with steam (Leuckart a. Hermann, *B.* 20, 29).

Di-chloro-toluquinoxaline $C_9H_6N_2Cl_2$ *i.e.*



$C_6H_3Me<\begin{matrix}N:CCl\\ N:CCl\end{matrix}>$. [115°].

From di-oxy-toluquinoxaline (1 mol.) and PCl_5 (2 mols.) at 170° (Hinsberg, *A.* 237, 350). Needles (from chloroform and petroleum-ether). Insol. water.

DI-CHLORO-TOLUYL-BENZOIC ACID $CH_3.C_6H_4.CO.C_6H_2Cl_2.CO_2H$. *Di-chloro-phenyl tolyl ketone carboxylic acid.* From (β)-dichloro-phthalic anhydride, toluene, and Al_2Cl_6 (Le Royer, *A.* 238, 357).

CHLORO-(α)-TOLUYLIC ACID *v.* CHLORO-PHENYL-ACETIC ACID.

DI-CHLORO-DITOLYL $[3:4:1]C_6H_3MeCl.C_6H_3MeCl[1:3:4]$. [51°]. From di-amido-ditolyl by Sandmeyer's reaction (Stolle, *B.* 21, 1096). Laminæ (from alcohol). CrO_3 gives chloro-toluic acid [205°].

CHLORO-DI-TOLYL-*tert*-BUTYL ALCOHOL $CCl(C_6H_4Me)_2.CMe_2OH$. (c. 265°). From acetone-chloroform, toluene, and Al_2Cl_6 (Willgerodt a. Genieser, *J. pr.* [2] 37, 369).

Di-chloro-tolyl-*tert*-butyl alcohol $CCl_2(C_6H_4Me).CMe_2OH$. (c. 245°). From acetone-chloroform, toluene, and Al_2Cl_6 (W. a. G.).

CHLORO-TOLYLENE-*m*-DIAMINE $C_6H_2(CH_3)Cl(NH_2)_2$ [1:4:3:5]. [111°]. Formed by reduction of chloro-di-nitro-toluene [48°]. Gives the chrysoidine and Bismarck-brown reactions (Hönig, *B.* 20, 2420).

(β)-Di-chloro-tolylene-diamine $C_6H(CH_3)Cl_2(NH_2)_2$[1:2:4:5:6]. [110°]. Formed by reducing (β)-di-chloro-di-nitro-toluene [102°] (Seelig, *A.* 237, 164). Plates (from ligroin). On boiling with HOAc for twenty-five hours the anhydro- base is formed [170°]; brownish needles (from alcohol).

(α)-Tri-chloro-tolylene-diamine $C_6(CH_3)Cl_3(NH_2)_2$. [196°]. Formed by reduction of tri-chloro-di-nitro-toluene [227°] (Seelig, *B.* 18, 422; *A.* 237, 143). White needles (from alcohol). CrO_3 oxidises it to a quinone.

Acetyl derivative $C_6(CH_3)Cl_3(NAc_2)_2$. [220°].

(β)-Tri-chloro-tolylene-diamine $C_6(CH_3)Cl_3(NH_2)_2$. [207°]. Formed by reducing tri-chloro-di-nitro-toluene [141°] with stannous chloride in alcoholic solution (Seelig, *A.* 237, 143). Needles (from petroleum ether). On boiling with HOAc an anhydro- base is formed, hence the substance is an orthodiamine.

ω-CHLORO-DI-TOLYL-ETHANE $CH_2Cl.CH(C_6H_4.CH_3)_2$. From $CH_2Cl.CHCl.OEt$ (di-chloro-ether), toluene, and H_2SO_4 (Hepp, *B.* 7, 1413). Alcoholic KOH gives $CH_2:C(C_6H_4Me)_2$.

Tri-ω-chloro-di-tolyl-ethane $CCl_3.CH(C_6H_4.CH_3)_2$. [89°]. S. (ether) 50; (alcohol) 2·5. From chloral, toluene, and H_2SO_4 (O. Fischer, *B.* 7, 1191).

DI-CHLORO-DI-TOLYL ETHYLENE $CCl_2:C(C_6H_4.CH_3)_2$. [92°]. S. (ether) 50; (alcohol) 2·9. From the preceding body and alcoholic KOH (O. Fischer, *B.* 7, 1191). Needles.

DI-CHLORO-DI-TOLYL-METHANE $CH_2(C_6H_4.CH_2Cl)_2$. [108°]. From benzyl chloride, methylal $CH_2(OMe)_2$, and H_2SO_4. Laminæ (Weiler, *B.* 7, 1181).

***o*-CHLORO-*m*-TOLYL-PHENYL-THIO-UREA** $C_6H_5.NH.CS.NH.C_6H_3MeCl$ [5:1:2]. [109°]. White granules. From $C_6H_3MeCl(NH_2)$[1:2:5] and phenyl-thiocarbimide (Goldschmidt a. Hönig, *B.* 20, 201).

CHLORO-TROPIC ACID $C_9H_9ClO_3$ *i.e.* $C_6H_5.CCl(CO_2H).CH_2OH$. [128°-130°]. From atropic acid and HClO (Ladenburg a. Rügheimer, *A.* 217, 109). V. e. sol. water, sl. sol. benzene. Reduced by zinc-dust, iron filings, and KOH to tropic acid.

CHLOROUS. Adjective sometimes used as synonymous with *negative* or *acidic*; generally applied to radicles which combine with *basylous* radicles to form salts, *e.g.* the radicles SO_3, N_2O_5, ClO_2 are called *chlorous*, as distinguished from K_2O, CaO, &c., which are basylous. The term chlorous is also sometimes applied to the more negative elements, especially to those which, like chlorine, do not displace the H of acids to form salts. The correlative term is *basylous*.

M. M. P. M.

CHLOROUS ACID $HClO_2$; *v.* CHLORINE, OXY-ACIDS OF, p. 17.

α-CHLORO-ISOVALERIC ACID $C_5H_9ClO_2$ *i.e.* $(CH_3)_2CH.CHCl.CO_2H$. From sodium isovalerate and aqueous HOCl (Schlebusch, *A.* 141, 322). Oil; decomposed by heat.

Tri- and tetra-chloro-isovaleric acids were obtained by Dumas a. Stas by chlorinating isovaleric acid in the dark. They decompose between 110° and 150°, giving off HCl.

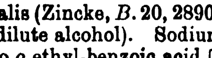
CHLORO-ISOVALERIC ALDEHYDE C_5H_9ClO. (135°). S.G. ^{14} 1·108. From isovaleric aldehyde and Cl at −18° (Schröder, *B.* 4, 402). Combines with $NaHSO_3$.

Di-chloro-isovaleric aldehyde $C_5H_8Cl_2O$ (147°). From isovaleric aldehyde and Cl at 15°. Combines with $NaHSO_3$ (Kundig, *A.* 114, 1).

TRI-CHLORO-VALEROLACTIC ACID *v.* TRI-CHLORO-OXY-VALERIC ACID.

CHLORO-VALERO-LACTONE *v.* CHLORO-OXY-VALERIC ACID, *Anhydride of.*

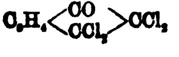
DI-CHLORO-VALERYLENE $C_5H_6Cl_2$ *i.e.* $CH_2:CCl.CH_2.CCl:CH_2$. *Di-chloro-di-vinyl-methane.* (145°). Formed by the action of PCl_5 upon acetyl-acetone. Liquid; boils without decomposition. Readily takes up Br, forming $C_5H_6Cl_2Br_4$. Heated with alcoholic KOH it gives $CH:C.CH_2.C(OC_2H_5):CH_2$ (Combes, *A. Ch.* [6] 12, 222).

DI-CHLORO-*o*-VINYL-BENZOIC ACID $C_2HCl_2.C_6H_4.CO_2H$. [121°]. From tri-chloro-oxy-indonaphthene  $C_6H_4<\begin{matrix}CO\\ CHCl\end{matrix}>CCl_2$ by solution in aqueous alkalis (Zincke, *B.* 20, 2890). Slender needles (from dilute alcohol). Sodium amalgam converts it into *o*-ethyl-benzoic acid [68°].

Methyl ether MeA′. [47°].

***o*-*Exo*-tri-chloro-vinyl-benzoic acid** $C_6H_4(CCl:CCl_2)CO_2H$[1:2]. [161°].

Formation.—1. By the action of NaOHAq on tetra-chloro-oxy-indonaphthene



$C_6H_4<\begin{matrix}CO\\ CCl_2\end{matrix}>CCl_2$ (Zincke, *B.* 20, 2055).

2. Tetrachloro (β)-naphtho-quinone is dissolved in NaOHAq, HOAc added, and the mixture oxidised with chromic acid (Zincke, *B.* 21, 499).

Properties. Needles or plates. V. sol. alcohol and HOAc. Sodium amalgam yields *o*-ethyl benzoic acid.

Methyl ether A'Me. [75°].

CHLORO-VINYL ETHYL OXIDE C_4H_7ClO *i.e.* $CH_2:CCl.OEt$ (123°). S.G. ^{24} 1·02 (Geuther); ^{12} 1·036 (Godefroy). V.D. 3·52. From tri-chloro-ethane $CH_3.CCl_3$ and NaOEt at 120° (Geuther, *Z.* 1871, 128). Formed also by the action of zinc-dust or the zinc-copper couple on the compound $C_6H_{12}Cl_2O_4$ obtained by passing chlorine through a mixture of alcohol and $K_2Cr_2O_7$ (Godefroy, *C. R.* 102, 869).

Reactions.—1. Br forms $CH_2Br.CClBr.OEt$ (170°–180°), whence Cl forms $CH_2Cl.CCl_2.OEt.$—2 HCl forms $CH_2Cl.CHCl.OEt.$—3. HNO_3 gives acetic and chloro-acetic acids. 4. Reduces ammoniacal $AgNO_3$, forming a mirror. 5. Exposed to the air it rapidly changes to a vitreous mass $(C_4H_7ClO)_3$aq.

Di-chloro-vinyl ethyl oxide $CHCl:CCl.OEt.$ (128° cor.). S.G. ^{10} 1·08. Formed by the action of NaOEt upon $CH_2Cl.CHCl_2$ (Geuther a Brockhoff, *J. pr.* [2] 7, 112) or $CClH:CCl_2$ (Paternò a. Oglialoro, *B.* 7, 81). Water at 180° forms glycollic acid.

Di-chloro-vinyl ethyl oxide $CCl_2:CH.OEt.$ (145°). From $CHCl_2.CHCl.OEt$ and conc. aqueous KOH (Godefroy). Sweet-smelling oil. Reduces ammoniacal $AgNO_3$, forming a mirror. Greedily combines with Br.

Tri-chloro-vinyl ethyl oxide $CCl_2:CCl.OEt.$ (155°) (B.); (c. 160°) (G.). S.G. ^{0} 1·373; ^{100} 1·235 (P. a. P.); ^{19} 1·332 (G.).

Formation.—1. From $CCl_2:CCl_2$ and NaOEt at 110° (Geuther a. Fischer, *J.* 1864, 316).—2. From $CCl_3.CHCl.OEt$ and conc. aqueous KOH (Paternò a. Pisati, *G.* 2, 333; Godefroy, *C. R.* 102, 869; Busch, *B* 11, 146). Smells like mint. Br forms $CCl_2Br.CClBr.OEt$ [17°]. Cl gives $C_2Cl_5.O.C_2H_5$.

CHLORO-DI-VINYL-METHANE *v.* DI-CHLORO-VALERYLENE.

HEXA-CHLORO-DI-VINYL OXIDE C_4Cl_6O *i.e.* $(CCl_2:CCl)_2O$. *Chloroxethose.* (210°). S.G. ^{21} 1·652. From $(C_2Cl_5)_2O$ and alcoholic K_2S (Malaguti, *A. Ch.* [3] 16, 19). Br forms $C_4Cl_6Br_4O$ [96°]

CHLOROX- *v.* CHLORO-OX-.

CHLOROXAL- *v.* CHLORO-OXAL-.

CHLOROXETHOSE *v.* HEXA-CHLORO-DI-VINYL OXIDE.

CHLOROXY- *v.* CHLORO-OXY-.

CHLORO-*o*-XYLENE $C_6H_3(CH_3)_2Cl$ [1:2:3]. Mol. w. 140½. (190° cor.). Fluid at −10°. Formed, together with the (1:2:4)-isomeride, by chlorination of *o*-xylene in presence of 5 p.c. of iodine. By dilute HNO_3 it is oxidised to chloro-toluic acid [154°], which by $KMnO_4$ is further oxidised to chloro-phthalic acid [181°] (Krüger, *B.* 18, 1755).

Chloro-*o*-xylene $C_6H_3(CH_3)_2Cl$ [1:2:4]. (192° cor.) Fluid at −20°. S.G. $\frac{15}{15}$ 1·0692. Formed, together with the (1:2:3)-isomeride, by chlorination of *o*-xylene in presence of 5 p.c. of iodine. By dilute HNO_3 it is oxidised to two isomeric chloro-toluic acids [166°] and [130°], which by further oxidation with $KMnO_4$ yield chloro-phthalic acid [130°–134°] (Krüger, *B.* 18, 1755).

Chloro-*o*-xylene $C_6H_3(CH_3)_2Cl$. (205° uncor.) S.G. ^{12} 1·0863. Colourless, strongly refractive liquid. According to Claus a. Kautz (*B.* 18, 1367) this is the only chloro-*o*-xylene formed by chlorination of *o*-xylene in the cold in presence of iodine. It is readily oxidised by dilute HNO_3 to chloro-phthalic acid.

Chloro-*m*-xylene $C_6H_3(CH_3)_2Cl$ [1:3:4]. (186° cor.). S.G. $\frac{20}{20}$ 1·0598. Fluid at −20°. Formed by chlorination of *m*-xylene in presence of 5 p.c. of iodine. By $K_2Co_2O_7$ and H_2SO_4 it is oxidised to chloro-*m*-toluic acid $C_6H_3(CH_3)Cl.CO_2H$ [3:4:1] of melting-point [210°] (Jacobsen, *B.* 18, 1760; *cf.* Vollrath, *Z.* 1866, 488).

Chloro-*p*-xylene $C_6H_3(CH_3)_2Cl$ [1:4:2]. [+2°]. (186° cor. at 767 mm.). Formed by chlorination of *p*-xylene in presence of I (Kluge, *B.* 18, 2099).

ω-Chloro-*o*-xylene $C_6H_4(CH_3)(CH_2Cl)$ [1:2]. (198°).

Formation.—1. By chlorinating boiling *o*-xylene (Reyman, *Bl.* [2] 26, 534).—2. By heating $C_6H_4(CH_3)(CH_2OH)$ [1:2] with conc. HCl. It cannot, however, be obtained pure in this way (Colson, *A. Ch.* [6] 6, 117).

Reaction.—Boiling aqueous $Pb(NO_3)_2$ gives *o*-toluic aldehyde.

ω-Chloro-*m*-xylene $C_6H_4(CH_3)(CH_2Cl)$ [1:3]. So-called *m-Tolyl chloride.* (196°). S.G. ^{0} 1·079.

Formation.—1. From Cl and boiling *m*-xylene (Vollrath; Lauth a. Grimaux, *Bl.* [2] 7, 233; *A.* 145, 115; Gundelach, *C. R.* 82, 1441) 2. By the action of HCl upon $C_6H_4(CH_3).(CH_2OH)$ [1:3] (Colson, *A. Ch.* [6] 6, 118).

ω-Chloro-*p*-xylene $C_6H_4(CH_3)(CH_2Cl)$ [1:4]. (192°). From Cl and boiling *p*-xylene (L. a. G.).

Di-chloro-*o*-xylene $C_6H_2(CH_3)Cl_2$. [3°]. (227°). Colourless strongly refractive liquid. Formed by chlorination of *o*-xylene in the cold in presence of iodine. It is readily oxidised by dilute HNO_3 to di-chloro-phthalic acid [183°] (Claus a. Kautz, *B.* 18, 1367).

Di-chloro-*m*-xylene $C_6H_2(CH_3)_2Cl_2$. (222°). From *m*-xylene and Cl in presence of iodine (Hollemann, *Z.* 1865, 554; *A.* 144, 268). White laminæ; melts by the heat of the hand.

Di-chloro-*p*-xylene $C_6H_2(CH_3)_2Cl_2$ [1:4:2:5]. [71°]. (221° i. V.).

Formation.—1. By chlorination of *p*-xylene. 2. From chloro-*p*-xylidine [92°] by diazotisation and treatment with Cu_2Cl_2 (Kluge, *B.* 18, 2098). Plates or flat needles. V. sol. hot alcohol and ether, sl. sol. cold alcohol.

ωω-Di-chloro-*o*-xylene $(1.2)C_6H_4(CH_2Cl)_2$. [55°]. (240°). S.G. ^{0} 1·393. S.H. (15° to 40°) ·283.

Formation.—1. By the action of HCl on ωω-di-oxy-*o*-xylene (Hessert, *B.* 12, 648; Colson, *Bl.* [2] 43, 7).—2. By heating *o*-xylene (10 c.c.) with PCl_5 (35 g.) at 180°–200° (Colson a. Gautier, *Bl.* [2] 45, 6; *C. R.* 101, 1064; 104, 428; Strassmann, *B.* 21, 578).

Properties.—White crystals; v. sol. ether, alcohol, ligroïn, and chloroform. Converted by heating with water into $C_6H_4(CH_2OH)_2$ [62°]. Potassium phthalimide reacts with formation of $CH_2Cl.C_6H_4.CH_2.N:C_8H_4O_2$ [140°] (Strassmann, *B.* 21, 576).

Di-chloro-*o*-xylene $C_6H_4(CH_3)(CHCl_2)$ (?). [103°]. (225°). From Cl and boiling *o*-xylene (Reyman, *Bl.* [2] 26, 534)

ω-Di-chloro-*m*-xylene $C_6H_4(CH_2Cl)_2$[1:3]. [34°]. (253°). S.G. ^{20} 1·302. S.H. (15° to 40°) ·295.

Formation.—1. From $C_6H_4(CH_2OH)_2$ [1:3] and HCl (Colson, *Bl.* [2] 43, 7). By heating *m*-xylene at 180° with the equivalent amount of PCl_5. The yield is not so good as with the *o*- and *p*-compounds, and to obtain it pure it is necessary to saponify the crude product and treat the glycol so produced with HCl (Colson a. Gautier, *Bl.* [2] 45, 6; *A. Ch.* [6] 6, 114).

Di-ω-chloro-*p*-xylene $C_6H_4(CH_2Cl)_2$ [1:4]. [100°]. (240°–250°). S.G. ^{0} 1·417. S.H. (15° to 40°) ·282.

Formation.—1. From Cl and boiling *p*-xylene (Lauth a. Grimaux, *A.* 145, 115).—2. From $C_6H_4(CH_2OH)_2$ [1:4] and HCl.—3. By heating *p*-xylene at 180° with the equivalent amount of PCl_5 (Colson a. Gautier, *Bl.* [2] 45, 6).

Properties.—Tables (from alcohol). Heated with water it gives the glycol $C_6H_4(CH_2OH)_2$. [113°] (Grimaux, *C. R.* 70, 1363).

Tri-chloro-*o*-xylene $C_6H(CH_3)_2Cl_3$. [93°]. (265° uncor.). Formed by chlorination of *o*-xylene in the cold in presence of iodine (Claus a. Kautz, *B.* 18, 1367). Long colourless glistening needles. V. sol. ether, benzene, hot acetic acid, and hot alcohol, v. sl. sol. cold alcohol. It is readily oxidised by dilute HNO_3 to tri-chlorophthalic acid, the anhydride of which melts at [157°].

Tri-chloro-*m*-xylene $C_6H(CH_3)_2Cl_3$. [150°]. (255°). From *m*-xylene and Cl in presence of iodine (Hollemann, *A.* 144, 270). Silky needles: v. sol. hot, sl. sol. cold, alcohol.

Tetra-chloro-*o*-xylene $C_6(CH_3)_2Cl_4$. [215° uncor.]. Formed by chlorination of *o*-xylene in the cold in presence of iodine (Claus a. Kautz, *B.* 18, 1367). Sublimable. Long colourless needles. Not volatile with steam. Sol. ether, benzene, hot acetic acid, and hot alcohol, sl. sol. cold alcohol. It is not oxidised by heating with HNO_3.

Tetra-ω-chloro-*o*-xylene $C_6H_4(CHCl_2)_2$ [1:2]. [86°] (C. a. G.); [89°] (H.). (274°). S.G. ^{0} 1·601. S. (ether) 50 at 15°; 100 at 35°. S.H. (15°–60°) ·24.

Formation.—1. From Cl and boiling *o*-xylene (Hjelt, *B.* 18, 2879).—2. From PCl_5 and *o*-xylene at 150° (Colson a. Gautier, *Bl.* [2] 45, 10).

Properties.—Triclinic crystals (from ether) $a{:}b{:}c = {·}972{:}1{:}{·}741$; $\alpha = 54°\ 38'$; $\beta = 54°\ 20'$; $\gamma = 58°\ 24'$. Its solubility in petroleum ether is double that of the *p*-compound. Sol. C_6H_6, $CHCl_3$, and alcohol. Water at 170° converts it into phthalide.

Tetra-ω-chloro-*m*-xylene $C_6H_4(CHCl_2)_2$. (273°). S.G. 1·536 (Colson a. Gautier, *Bl.* [2] 45, 509).

Tetra-ω-chloro-*p*-xylene $C_6H_4(CHCl_2)_2$ [1:4]. [93°]. S.G. ^{0} 1·606. S.H. (15° to 60°) ·242. S. (ether) 50 at 35°; S. (ligroïn) 7. Formed by heating *p*-xylene ($5\frac{1}{2}$ c.c.) and pure PCl_5 (40 g.) at 195°, and crystallising the product from ether (Colson a. Gautier, *Bl.* [2] 45, 9). Saponified by boiling with water gives terephthalic aldehyde $C_6H_4(COH)_2$ [1:4]. [114°].

Penta-ω-chloro-*o*-xylene $C_6H_4(CCl_3)(CHCl_2)$ [1:2]. [54°]. From *o*-xylene (3·2 c.c.) and PCl_5 (40 g.) at 200° (Gautier a. Colson, *C. R.* 102, 689). Converted by boiling water into $C_6H_4(CO_2H)(CHO)$. [97°].

Hexa-chloro-*m*-xylene $C_8H_4Cl_6$ [1:3]. (c. 286°) From *m*-xylene and PCl_5 (Colson a. Gautier, *C. R.* 102, 689). Converted by alkalis into a chlorinated acid.

Hexa-ω-chloro-*p*-xylene $C_6H_4(CCl_3)_2$ [1:4]. [111°]. Formed by heating *p*-xylene (1 mol.) with PCl_5 (6·5 mol.) for 10 hours at 200°. Transparent crystals. Sol. ether. Heated with a solution of NaHO, it loses all its chlorine, forming terephthalic acid (Colson a. Gautier, *Bl.* [2] 45, 507).

CHLORO-*o*-XYLENE-SULPHONIC ACID $C_6H_2(CH_3)_2Cl.SO_3H$ [1:2:4:5]. Formed by sulphonation of chloro-*o*-xylene (1:2:4) (Kruger, *B.* 18, 1756). On reduction with sodium amalgam it gives *o*-xylene-sulphonic acid (1:2:4).

Salts.—A'Na 5aq: glistening needles or large flat prisms.—A'K: short needles.—A'_2Ba 4aq: long needles, sol. hot water, more sparingly in cold.

Amide $C_6H_2Me_2Cl.SO_2NH_2$: [207°]; long felted needles, sol. hot, sl. sol. cold, alcohol, v. sl. sol. water.

Chloro-*o*-xylene-sulphonic acid $C_6H_2(CH_3)_2Cl.SO_3H$ [1:2:3:6]. Formed by sulphonation of chloro-*o*-xylene (1:2.3) (Krüger, *B.* 18, 1756).

Salts.—A'Na aq: large pearly plates.—A'K: plates.—A'_2Ba aq: thin glistening plates.

Amide $C_6H_2Me_2Cl.SO_2NH_2$: [199°]; fine silky needles or long prisms, sol. hot alcohol, sl. sol. water.

Chloro-*m*-xylene-sulphonic acid $C_6H_2(CH_3)_2Cl.SO_3H$ [1:3:4:6]. Formed by sulphonation of chloro-*m*-xylene, $C_6H_3(CH_3)_2Cl$ [1:3:4] (Gundelach, *Bl.* [2] 28, 343; Jacobsen, *B.* 18, 1761).

Salts.—A'Na aq: long fine needles, sl. sol. cold water.—A'K aq: needles, v. e. sol. water.—A'_2Ba very sparingly soluble small tables.

Amide $C_6H_2(CH_3)_2Cl.SO_2NH_2$. [195°]. Prisms (from alcohol).

Chloro-*p*-xylene-sulphonic acid $C_6H_2(CH_3)_2Cl.SO_3H$. Formed by sulphonation of chloro-*p*-xylene.

Salts.—A'Na aq; easily soluble prisms.—A'_2Ba aq: sparingly soluble needles (Kluge, *B.* 18, 2099).

CHLORO-*m*-XYLIDINE $C_8H_{10}ClN$. [89°]. From (2,3,1)-nitro-*m*-xylene, tin, and HCl (Tavildaroff, *Z.* 1870, 419). Crystalline.

Chloro-*p*-xylidine $C_6H_2(CH_3)_2Cl.NH_2$ [1:4:2:5]. [92°]. Formed by the action of tin and HCl upon nitro-*p*-xylene (Jannasch, *A.* 176, 55). Laminæ (from water). By diazotising and treatment with cuprous chloride it yields di-chloro-*p*-xylene [71°].

Salts.—B'HCl 2aq.—$B'_2H_2SO_4$ 2aq.—$B'_2H_2C_2O_4$.

Acetyl derivative $C_6H_2Me_2Cl.NHAc$—[171°], colourless needles (Kluge, *B.* 18, 2098).

CHLORO-XYLO-HYDROQUINONE *v.* CHLORO-HYDRO-XYLOQUINONE.

CHLORO-XYLOQUINONE $C_6HClMe_2O_2$ [*x*:1:4:2:5]. *Chloro-phlorone.* [48°]. Conc. HCl dissolves xyloquinone, but immediately a brown crystalline mass separates. This is a mixture of mono- and di-chloro-hydro-xyloquinones. If it be oxidised by CrO_3 or HNO_3, a mixture of mono- and di-chloro-xyloquinones is got. From alcohol the former crystallises in needles, the latter in plates (Carstanjen, *J. pr.* [2] 23. 430; *cf.* V. Rad, *A.* 151, 158). Chloro-xyloquinone is converted by boiling with HCl into di-chloro-hydro-xyloquinone.

Di-chloro-xyloquinone $C_6Cl_2Me_2O_2$. [175°]. Prepared as above. Not affected by boiling HCl.

α-DI-CHLORO-*o*-XYLYLENE-DI-MALONIC ETHER $C_6H_4[CH_2.CCl(CO_2Et)_2]_2$. From sodium chloro-malonic ether and $[1:2]C_6H_4(CH_2Br)_2$ (Baeyer a. Perkin, *B.* 17, 452; *C. J.* 53, 14). Liquid. Alcoholic KOH gives *o*-phenylene-di-acrylic acid.

Di-chloro-*m*-xylylene-di-malonic ether $C_6H_4(CH_2.CCl(CO_2Et)_2)_2$. Formed by the action of chloro-malonic ethyl ether and sodium ethylate on *m*-xylylene dibromide (Kipping, *C. J.* 53, 26). Thick yellowish oil.

Di-chloro-*p*-xylylene-di-malonic ether $C_6H_4[CH_2.CCl(CO_2Et)_2]_2$. [87°]. Formed by acting with ethyl chloromalonate and sodium ethylate on *p*-xylylene dibromide (Kipping, *C. J.* 53, 35). Colourless six-sided plates. Insol. water, v. sol. alcohol, ether, petroleum ether, and HOAc.

CHLORO-DI-XYLYL-ETHANE $C_{18}H_{21}Cl$ *i.e.* $CH_2Cl.CH(C_6H_3Me_2)_2$. From di-chlorinated ether $CH_2Cl.CHCl.OEt$, xylene, and H_2SO_4 (Hepp, *B.* 7, 1416). On distillation it splits up into HCl and $CH_2:C(C_6H_3Me_2)_2$.

CHOLALIC ACID *v.* CHOLIC ACID.

CHOLANIC ACID $C_{25}H_{38}O_7$ ½aq. [285°] (L.). S. ·025 at 100°; ·011 at 20° (L.; *cf.* Kutscheroff, *B.* 14, 1492); S. (alcohol of 98·5 p.c. at 18°) 1·37. $[\alpha]_D = 53°$ (T.); 88° (Kutscheroff). Formed by oxidation, with $K_2Cr_2O_7$ and H_2SO_4, of choleic acid $C_{25}H_{42}O_4$, of dehydrocholeic acid $C_{25}H_{38}O_4$, and also (according to L.) of desoxycholic acid (Tappeiner, *A.* 194, 231; Latschinoff, *B.* 13, 1052; 18, 3045; 19, 474, 1521; 20, 1044; *Bl.* [2] 46, 818). Large tables or flat prisms. Tribasic acid. Dextro-rotatory. On further oxidation by boiling with HNO_3 (1·28 S.G.), it gives choloidanic acid and pseudo-choloidanic acid.

Salts.—A'''_2Ba_3 6aq: tables or plates; S. (at 18°) 4·12; $[\alpha]_D = +49·37°$.

Mono-methyl ether $A'''H_2Me$: [207°]; very slender needles; v. sol. alcohol, less sol. ether; the Na, K, Ca, and Ba salts are v. sol. water and alcohol.—A'''MeBa.

Mono-ethyl ether $A'''H_2Et$: [190°]; the properties are the same as those of the mono-methyl ether.—A'''EtBa. A'''EtPb.

Di-methyl ether $A'''HMe_2$: [176°]; needles.

Di-ethyl ether $A'''HEt_2$: [131°].—A'''_2Et_4Ba.—A'''_2Et_4Pb.

Tri-methyl ether $A'''Me_3$: [121°]; needles.

Tri-ethyl ether $A'''Et_3$: [76°]; needles.

***Iso*-cholanic acid** $C_{25}H_{38}O_7$(?) [248°]. $[\alpha]_D = 73·3°$. S. ·022; S. (alcohol) 9·1; S. (ether) ·018. Formed in small quantity, together with cholanic acid, by oxidation of choleic acid, with $K_2Cr_2O_7$ and H_2SO_4 (Latschinoff, *B.* 15, 713; 19, 1529). The cholanic acid described by Tappeiner appears to be contaminated with a small quantity of this isomeric acid. Pearly plates. Penta-basic acid.

Salts.—A^vK_5: soluble hair-like needles.—$A^vK_2H_3$: fine needles.—$A^v_2Ba_3$ 10aq?: sparingly soluble amorphous powder.—A^vBa_2H.—$A^v_2Pb_5$ 6aq: amorphous pp., insol. water and alcohol.—A^vAg_5: insoluble amorphous pp. $A^v_2Cu_3Cu_4O_4$ 10aq: amorphous blue pp.

Methyl ether $C_{25}H_{33}O_7Me_5$: [136°]; plates. From the lead salt and MeI.

Ethyl ether $C_{25}H_{33}O_7Et_5$: [43°–50°]; flat needles.

CHOLECAMPHORIC ACID *v.* CHOLOÏDANIC ACID.

CHOLEÏC ACID $C_{25}H_{42}O_4$(?). [185°–190°]. S. (water at 20°) ·0045; (75 p.c. alcohol at 20°) 4; (absol. alcohol at 20°) 7·1; (absol. ether at 20°) ·133. With 300 mm. of a 6·06 p.c. solution in absol. alcohol at 20°, $[\alpha]_D = 56°40'$. From alcohol or acetic acid it crystallises in hemihedral rhombic needles, $a:b:c = 1:·5057:1·8598$.—Occurs in saponified ox-gall together with cholic and desoxycholic acids. It gives Pettenkofer's test for bile acids (Mylius, *H.* 11, 492). On gentle oxidation with CrO_3 and acetic acid it is converted into dehydrocholeic acid $C_{25}H_{38}O_4$, by more vigorous oxidation, with $K_2Cr_2O_7$ and H_2SO_4, into cholanic acid (but no bilianic acid). According to Latschinoff by boiling with glacial acetic acid it is converted into desoxycholic acid (called by him 'hydrated choleic acid'); Mylius, however, was unable to confirm this statement.

Salts.—A′Ag.—A'_2Ba: microscopic plates, insol. strong alcohol and water, v. sol. dilute alcohol forming the hydrated salt.—A'_2Ba 6aq: needles, v. sol. dilute alcohol, S. (water at 20°) ·083 (Latschinoff, *Bl.* [2] 46, 817; *B.* 18, 3039; 19, 1140; 20, 1043, 1053; Mylius, *B.* 19, 369; 20, 1968).

Dehydrocholeic acid $C_{25}H_{38}O_4$ (?) according to L. [183° uncor.]. Obtained by slowly adding a 10 p.c. solution of CrO_3 (3 pts.) in acetic acid to a 10 p.c. solution of choleic acid (4 pts.) in acetic acid; the yield is 60 to 70 p.c. According to L. it is also formed by similar treatment from desoxycholic acid. Silky tables. Less soluble in water and alcohol than dehydrocholic acid. By further oxidation with $K_2Cr_2O_7$ and H_2SO_4 it yields cholanic acid.—$A''Ba$ 1½aq: needles, v. sol. alcohol, sl. sol. water (Latschinoff, *B.* 18, 3045; 20, 1044).

CHOLESTERIN (*Animal cholesterin*) $C_{26}H_{44}O$,aq, or $C_{25}H_{42}O$,aq, or $C_{27}H_{46}O$aq. [146°, Hesse] [147·5°, or cor. = 148·5°, Reinitzer] [usually given at 145° to 146°].[1] $[\alpha]_D$ for anhydrous cholesterin from gallstones in chloroform = (−36·61 + 0·249 p.) (O. Hesse). This rotation depends to some extent on the strength of the solution. S.G. $\frac{0}{20}$ 1·046 (Mehu, *J. Ph.* [4] 20, 175); 1·067 (Hoppe-Seyler, *Gmelin's Handb.*, 18, 113); 1·03 after fusion (Hein., *ibid.*).

Occurrence.—This substance was first obtained by Conradi in 1755 from human gallstones, of which it sometimes constitutes nearly the entire substance. It has been found in human bile (Chevreul, *A. Ch.* 95, 5; 96, 166); in the blood (Lecanu, *A. Ch.* 67, 54; Boudet, *ibid.* 336; Denis, *J. Chim. Méd.* [2] 4, 161; Becquerel a. Bodier, *Gaz. Méd.* 47); together with protagon as an essential constituent of the nervous tissue, of the yolk of egg, of the seminal fluid, and of the red and white corpuscles of the blood (Hoppe-Seyler, *Med. Chem.*

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[1] When cholesterin is mixed with iso-cholesterin, the melting point is lowered.

Unters. 1, 140; *J.* 1866, 744): in the brain (Couerbe, *A. Ch.* 56, 281; Fremy, *ibid.* [3] 11, 486; Beneke, *Bied. Centr.* 1881, 568)—the brain of a boy 15 years old was found to contain 26·92 g. cholesterin = 2·34 p.c., that of a woman 19 years old, 26 79 g. = 2·12 p.c. (Beneke); in the yolk of egg (Lecanu, *J. Ph.* 15, 1; Gobley, *ibid.* [3] 12, 12 four hen's eggs yielded 0·592 g., and four newly hatched chickens 0·41 g. (Beneke); in oxen bile (Hüfner, *J. pr.* [2] 19, 305); in human milk to the amount of 0·0318 p.c. (Tolmatscheff, *Med.-Chem. Unters.* 1, 272); in cow's milk (Schmidt a. Mulheim, *Archiv f. d. ges. Physiol.* 25, 384); in the spleen, and abundantly in the excrements of the crocodile (Marcet, *A. Ch.* [3] 59, 91); in guano (Hoppe-Seyler, *J.* 1863, 654); in the corpus luteum of the cow (Lieben, *Z.* 4, 646); along with paracholesterin in the protoplasm of *ethalium septicum* (Reinke a. Rodewald, *A.* 207, 228); along with iso-cholesterin in the grease of sheep's wool (Hartmann, *Inaug. Dissert. Göttingen*, 1868; E. Schulze, *Z.* [2] 6, 153); and in certain morbid products of the animal economy, such as cerebral concretions, scirrhous matter of the mesocolon, hydropic liquid of the abdomen, ovaries, testicles, &c. (Lassaigne, *A. Ch.* 9, 324; O. Henry, *J. Chim. Med.* 1, 280; Caventou, *J. Ph.* 11, 462; Lehmann, *Lehrb. d. Physiol. Chem.* 2te Aufl. 1, 286).

The first exact analysis of cholesterin was made by Chevreul, who assigned to it the formula $C_{26}H_{44}O$. Its metamorphoses have been studied by Marchand (*J. pr.* 16, 37); Redtenbacher (*A.* 57, 145); Meissner a. Schwendler (*ibid.* 59, 107, also *J. pr.* 39, 247); Zwenger (*A.* 66, 5; 69, 347); Heintz (*P.* 79, 524); Berthelot (*A. Ch.* [3] 56, 51); and by others, who will be referred to in the course of this article.

Preparation.—1. By crystallising biliary calculi from boiling alcohol, to which a little potash is added to dissolve any fatty acids that may be present.—2. By extracting brain substance with ether, and boiling the evaporated extract with alcoholic potash.—3. From the grease of sheep's wool by saponifying for 20 hours at 100° with alcoholic potash in a closed stoneware bottle, evaporating the alcohol, taking up with water and shaking with ether. The residue from the evaporation of the ether consists of a mixture of cholesterin, iso-cholesterin, and a nearly-related amorphous alcohol poorer in carbon,[1] and these are best separated from one another by conversion into their benzoic ethers, by fusing the mixture of alcohols (2 parts) with benzoic anhydride (1 part) to about 180° for 48 hours. The resulting mass is rubbed up with a little alcohol in a mortar, treated first with a cold solution of Na_2CO_3, and then with warm water to extract the benzoic acid formed and the excess of anhydride, and then dried. To the mixture cold ether is now added, in which the benzoate of the amorphous alcohol is readily soluble, those of cholesterin and iso-cholesterin dissolving only slightly. The two latter may then be separated by slow recrystallisation from ether and elutriation, cholesterin benzoate crystallising in plates, and iso-cholesterin benzoate in needles. The benzoates are then separately saponified for their respective cholesterins, which are recrystallised for further purification (E. Schulze, *J. pr.* 7, 163).—4. On adding ether and HCl to fresh oxen bile, the cholesterin is obtained in the ethereal layer (Hüfner, *J. pr.* [2] 19, 305).

Properties.—Monatomic alcohol. Laminated transparent crystals of $C_{26}H_{44}O$,aq (from a mixture of alcohol (2 vols.) and ether (1 vol.)), which give off their water at 100°. Plates (containing aq) (from alcohol and ether). Anhydrous needles (from chloroform). Tasteless and inodorous. Insol. water, v. sol. hot, sl. sol. cold, alcohol, v. sol. ether, chloroform, carbon bisulphide, oil of turpentine, soap water, and neutral fats, &c.

Reactions.—(*a*) Sublimes at 200°, but decomposes at a higher temperature. (*b*) Resists the action of conc. alkaline solutions, even at the boiling temperature, but is decomposed by lime at about 250°, with evolution of hydrogen and formation of an amorphous body nearly insoluble in alcohol. (*c*) For the action of halogens *v.* Derivatives. (*d*) Yields with conc. H_2SO_4 a. b. and c. Cholesterilins (*v.* these) (Zwenger). (*e*) Yields with conc. H_3PO_4 (*a*) and (*β*) Cholesterones (*q.v.*).

Characteristic tests.—(*a*) When a few centigrammes are dissolved in chloroform and the solution is shaken up with an equal volume of H_2SO_4 (best of 1·76 S.G.), the chloroform layer, at first yellow-brown, soon becomes blood-red, and then cherry-red or purple, the colour remaining for some hours if the solution is in a closed bottle, *i.e.* if air be not admitted; it then becomes blue, green, and finally yellow. The sulphuric acid at the same time shows a fine green fluorescence (Hesse, *A.* 211, 283; Reinke a. Rodewald, *A.* 207, 229; Salkowski, *C. C.* 1873). (*b*) When a small quantity is evaporated at a gentle heat with a drop of nitric acid, a yellow spot is left, which turns red when touched with a drop of ammonia, and the red colour thus produced is not essentially altered by subsequent addition of fixed alkali, thus distinguishing this from the corresponding reaction with uric acid (Schiff, *A.* 115, 113). (*c*) When slowly evaporated to dryness with 3 vols. conc. HCl or H_2SO_4 and 1 vol. Fe_2Cl_6 solution, the particles remaining undissolved assume a violet-red colour, changing to bluish-violet at a somewhat higher, and dull-grey at a still higher, temperature. This reaction, which is likewise produced with $AuCl_3$, $PtCl_4$, or $K_2Cr_2O_7$ + HCl, is not exhibited by the colouring matter or any other constituent of the bile (Schiff).

Applications.—Cholesterin possesses the property of absorbing more than 100 p.c. of water (Liebrich, *cf.* *C. S. I.* 5, 578), a point of great therapeutic moment. The grease of sheep's wool is now therefore being purified in quantity, and the manufactured product, which is termed 'lanolin,' used as a basis for ointments, &c.

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[1] This amorphous alcohol, which is poorer in carbon than cholesterin, is v. sol. cold alcohol, ether, and acetone, but it has not yet been obtained pure, in fact there is as yet no guarantee that it is a chemically simple substance. It has a weak, aromatic odour, and melts at a gentle heat. It appears to be present in the fat, partly free and partly combined with acids, chiefly oleic. The greater portion of wool-fat consists of compound ethers, but a portion of the alcohols—at least of the cholesterins—and also sometimes a portion of the acids are present in the free state. The formation of potash soaps in wool-fat is now readily explained by the presence of free fatty acids on which the K_2CO_3 can act; a portion of the compound ethers may, however, be decomposed also (Schulze a. Urich. *J. pr.* [2] 8, 321).

Cholesteryl chloride, $C_{26}H_{43}Cl$. [97°, Walitzky]. [96°, Raymann]. Prepared by the action of PCl_5 on cholesterin or its acetate. Small scales, sl. sol. alcohol, v. sol. ether. Not decomposed by aqueous, but by boiling alcoholic potash (Planer, *A.* 118, 25; Lindenmeyer, *J. pr.* 90, 321; Rayman, *Bl.* [2] 47, 898).

Cholesterin dibromide $C_{26}H_{44}OBr_2$. Prepared by the action of bromine on cholesterin, both dissolved in CS_2. White needles (from ether-alcohol), sl. sol. alcohol, v. sol. ether. Is reconverted to cholesterin by Na amalgam (Wislicenus a. Moldenhauer, *A.* 146, 175).

Cholesteryl chloro-dibromide $C_{26}H_{43}Cl,Br_2$. [128°]. Prepared by gradually adding Br to an ethereal solution of cholesteryl chloride. White powder or large colourless crystals (from CS_2). Sol. carbon bisulphide, chloroform, and ligroin (Rayman).

Nitro-cholesterin [94°]. Red-yellow mass, insol. water, sol. NH_3Aq and K(Na)OHAq, v. sol. alcohol, ether, chloroform, &c. (Reinitzer, *M.* 9, 421).

Di-nitro-cholesterin $C_{26}H_{42}(NO_2)_2O$ or $C_{25}H_{40}(NO_2)_2O$. [121°]. Colourless needles (from alcohol). V. sol. hot alcohol and ether (Preis a. Rayman, *B.* 12, 224).

Nitro-cholesteryl chloride $C_{26}H_{42}(NO_2)Cl$ or $C_{25}H_{40}(NO_2)Cl$. [149°]. Colourless needles (from alcohol) (P. a. R.).

Cholesteryl acetate $C_{26}H_{43}O.C_2H_3O$ or $C_{27}H_{45}O.C_2H_3O$. [92°, Löbisch, *B.* 5, 513]; [113°, Raymann, *Bl.* 47] [111°–112° uncor. (chol. from gallstones), Jacobsen]; [114·5° cor.] (from gallstones) (Reinitzer, *M.* 9, 428).

Preparation.—By heating cholesterin, also sodium cholesterate, with acetic anhydride, or with acetic acid or acetyl chloride. Needles (from benzene). Trimorphous, the first modification being monosymmetric crystals, and the second monosymmetric plates with rhombic edges, while the third form has not yet been defined. Shows curious changes of colour on solidifying after fusion, which changes are not yet explained, but are apparently closely connected with the separation—during fusion—and resolution of a substance whose nature is not known (Leymann *v.* Reinitzer, *loc. cit.*).

Bromo-cholesteryl acetate $C_{27}H_{45}Br_2.C_2H_3O_2$. [118° cor. and 116° cor.] (Reinitzer, *M.* 9, 424).

Long glancing tables (from ether-alcohol). Dimorphous, the first modification being monosymmetric tables [118°], and the second asymmetric tables [116°]. Somewhat decomposed by light (Reinitzer).

Cholesteryl butyrate $C_{26}H_{43}O.C_4H_7O$. M. sol. hot alcohol.

Cholesteryl stearate $C_{26}H_{43}O.C_{18}H_{35}O$. Needles, sl. sol. cold ether, almost insol. alcohol (Berthelot).

Cholesteryl benzoate $C_{26}H_{43}O.C_7H_5O$ or $C_{27}H_{45}O.C_7H_5O$. [150°–151° Schulze; 146·6° cor. Reinitzer].

Preparation.—See separation of cholesterin and isocholesterin (Schulze, *J. pr.*). Better, by heating anhydrous cholesterin (10 pts.) with benzoic anhydride (12 pts.) in an open flask to 150°–160° for 1½ hours (Reinitzer, *M.* 9). Beautiful small glancing tables (from ether); m. sol. ether, sl. sol. boiling alcohol (Berthelot, Schulze). Trimorphous, the first modification being tetragonal crystals, the second forming rhombic needles or small plates, and the third crystallising in thin broad plates. Exhibits on fusion colour phenomena similar to those shown by the acetate, but not quite the same (Reinitzer, *loc. cit.*).

Sodium cholesterate $C_{26}H_{43}NaO$. [150°].

Formation.—By the action of Na on a saturated solution of cholesterin in petroleum. Silky needles (from petroleum or chloroform). Slowly decomposed by water, more quickly by alcohol (Lindenmeyer, *J. pr.* 90, 321).

Cholesterylamine $C_{26}H_{43}NH_2$. [104°] (Henry). Small plates.

Cholesteryl-aniline $C_{25}H_{41}.C_6H_5NH$. [187°].

Preparation.—By heating cholesterin chloride and aniline to 180° for 6–12 hours (Walitzky, *Chem. Sect. d. Russ. phys.-chem. Ges.*, Oct. 1878; *B.* 11, 1937). Long rectangular plates (from CS_2); m. sol. ether and boiling alcohol, v. sol. carbon bisulphide. Ppd. from ethereal solution by mineral acids.

Salts.—The H_2SO_4, HNO_3, and HCl salts are crystalline.

Cholesteryl-*p*-toluidine $C_{25}H_{41}NHC_7H_7$. [172°]. Prepared at 150°–180°. Rectangular tables (from ether). Sol. alcohol, ether, and carbon bisulphide. Weak base (Walitzky).

Salts.—The HNO_3 salt is much more stable than those of HCl or H_2SO_4.

Tri-oxy-cholesterin $C_{25}H_{42}O_3$.

Preparation.—(*a*) By saponifying the di-acetin (see below) with alcoholic potash, dissolving the residue in water and ppg. by an acid (Latschinoff, *Chem. Sect. d. Russ. phys.-chem. Ges.*, Oct. 1878; *B.* 11, 1941).

(*b*) By oxidising a solution of cholesterin in HOAc by $KMnO_4$; this latter method does not yield it quite pure.

Properties.—Yellowish powder. Sol. alcohol, ether, and KOHAq. Mol. w. not yet determined. Resembles phenol in behaviour.

Di-acetyl derivative $C_{25}H_{40}O(C_2H_3O_2)_2$. [77°].

Preparation.—Cholesterin acetate is oxidised by $KMnO_4$ and the di-acetin dissolved out of the resulting mass by ether (Latschinoff).

Properties.—White hard powder, indistinctly crystalline, obtained on adding water to the HOAc solution. V. sol. glacial acetic acid, alcohol, ether, benzene, &c., but not crystallisable from any one of these.

Cholesteriline *a*, *b*, and *c* $C_{26}H_{42}$ or $C_{25}H_{40}$ (Zwenger, *A.* 66, 5; 69, 347).

Preparation.—By acting with conc. H_2SO_4 on a slightly heated mixture of cholesterin and dilute sulphuric acid.

Properties.—(*a*) [240°]. Amorphous. Insol. water, almost insol. alcohol, v. sl. sol. ether. (*b*) [255°] shining scales. Insol. water, m. sol. hot ether. (*c*) [127°]. Resinous. Insol. water, sol. hot ether.

Walitzky's *Cholestene* $C_{26}H_{42}$, obtained by heating cholesterin with sodium to 150°–155°, appears to be identical with *c*, also with the compound obtained by acting on cholesterin with HI (S.G. 1·5), or by heating it with soda-lime up to 250°. Cholestene and the two last give, with excess of Br, the same compound $C_{26}H_{34}Br_8$ (Walitzky, *C. R.* 92, 195).

T. Weyl (*Archiv f. Anat. und Physiol.* 1, 182) has studied these compounds anew, and considers that they agree with the formula $(C_5H_8)_nH_2O$. For the relations between cholesterin, cholalic acid, and the terpenes, see Latschinoff, Walitzky, and Weyl.

Cholesterones $C_{26}H_{42}$ or $C_{25}H_{40}$. When cholesterin is boiled with excess of conc. phosphoric acid it forms two compounds, α- and β-cholesterone, isomeric with each other, but differing in physical properties (Zwenger, *A.* 69, 347).

α-Chloresterone. [68°]. Rectangular prisms, v. sol. alcohol and ether, and distilling without decomposition.

β-Cholesterone [175°]. Small silky needles, almost insol. alcohol, sl. sol. ether.

Cholesteric acid $C_{12}H_{16}O_7$.

Formation.—By the oxidation of cholic acid $C_{24}H_{40}O_5$ or $(C_{24}H_{40}O_5)_x$, by $K_2Cr_2O_7$ (10 parts) and H_2SO_4 (15 parts). The acid must be diluted with at least three times its volume of water before the oxidation, and the latter interrupted as soon as the cholesteric acid is formed, otherwise it is obtained mixed with pyro-cholesteric acid (see below). Redtenbacher's cholesteric acid $C_{16}H_{20}O_8$ (*A.* 57, 160) is such a mixture. The filtered solution must be concentrated at a low temperature, unless the H_2SO_4 is first neutralised. The cholesteric acid crystallises, and is purified either by washing with a little cold water or by recrystallisation from ether (Tappeiner, *A.* 194, 211; *B.* 12, 1627; Latschinoff, *B.* 12, 1518).

Properties.—Tribasic acid. Needles (from water and alcohol), long prisms (from ether containing some water). V. sol. hot water. Not volatile with steam. Slightly dextro-rotatory in alcoholic solution. Gives no colouration with sugar and H_2SO_4, and has not the toxic action of cholic acid. Its power of crystallisation is greatly diminished by the presence of small quantities of the pyro-acid.

Salts.—The Ca and Ba salts are less sol. hot than cold water. At 100° they generally go into salts of pyro-cholesteric acid (Tappeiner). A'''_2Ba_3, $A'''Ag_3$, $A'''H_2Ag$.

Pyro-cholesteric acid $C_{11}H_{16}O_5$. [108°].

Preparation.—(*a*) Best by heating a solution of cholesteric acid in glycerin for 5 to 8 days at 198°, saponifying the glycerates, distilling off small quantities of volatile acids, such as propionic, and extracting with ether (Tappeiner). (*b*) Also by boiling with H_2SO_4 diluted with 3 vols. water, but in this case the decomposition goes further.

Properties.—Gummy mass, sol. water, alcohol, and ether.

Iso-cholesterin $C_{26}H_{44}O$. [138°–138·5°]. $[\alpha]_D$ in ethereal solution + 60° (Schulze, *J. pr.* [2] 7, 163; Schulze a. Urich, *J. Pr.* [2] 9, 321; Schulze, *B.* 12, 249).

Occurrence.—In the fat of sheep's wool.

For *Preparation* and separation from cholesterin, see the latter.

Properties.—Flocks (from dilute alcoholic solution), a jelly (from concentrated alcoholic solution), fine transparent needles (from ether or acetone). Sl. sol. cold, v. sol. hot, alcohol, ether, and acetone, *i.e.* solubility is very much the same as that of cholesterin. A mixture of cholesterin and iso-cholesterin melts at a lower temperature than either separately.

Reactions.—(*a*) The $CHCl_3$ and H_2SO_4 test gives only a very feeble colouration (Schulze, *J. pr.* [2] 7, 168). (*b*) The HNO_3 and NH_3 test gives the same colouration as cholesterin.

Iso-cholesterin derivatives.

Iso-cholesteryl chloride $C_{26}H_{43}Cl$. Prepared by the action of PCl_5 on iso-cholesterin. Amorphous. V. sol. ether, sl. sol. alcohol.

Acetyl derivative [below 100°]. Amorphous; sl. sol. alcohol.

Stearyl derivative [72°]. Fine white needles (from ether). V. sl. sol. alcohol.

Benzoyl derivative $C_{26}H_{43}O.C_7H_5O$. [190°–191°]. Fine needles (from ether). Sl. sol. alcohol, m. sol. acetone, v. sol. ether.

Phytosterin $C_{26}H_{44}O$,aq. [132–133°] (Hesse, *A.* 192); [133°] (v. Lippmann, *B.* 20, 3201); [133°] Paschkis, *H.* 8, 356; [132°], [135°], [133°], and [136°], Jacobsen; [136–137°], Beneke; [136–137°] Schulze a. Barbieri (from lupines), *J. pr.* [2] 25, 159. $[\alpha]_D$ (anhydrous in $CHCl_3$)

= −34·2° (Hesse)
= −33·7° and −35·1° (*v.* Lippmann)
from −30·4 to −33·4 (Jacobsen)
−32·7° (Paschkis)
−32·5° in ether (Lindenmeyer)
−36·4° (Schulze a. Barbieri).

Those who first isolated phytosterin considered it to be cholesterin. The name phytosterin was given to it by Hesse.

Occurrence.[1]—In peas and olive oil (Beneke, *A.* 122, 249; Knop, *C. C.* 1862, 819); calabar beans (Hesse, *A.* 192, 176); in the seeds and cotyledons of the shoots of the yellow lupine, '*Lupinus luteus*' (Schulze a. Barbieri, *J. pr.* [2] 25, 159); in almonds; mustard seed; Bockshorn seed; in numerous fungi, *e.g. Polyponis officinalis* (Schmieder, *C. C.* 86, 774); in the seed oil of rape, lentils, almond, cotton, earth nut or pea nut, poppy, and cocoa (Salkowski, *Z. f. Anal. Chem.* 26, 557); together with cholesterin in butter and cod-liver oil (Salkowski); in hog's beans and vetches (Jacobsen); in the juice of beet (v. Lippmann, *B.* 20, 3201); in wheat gluten (Ritthausen, *J. pr.* 85, 212; 88, 145); in maize grains (Hoppe-Seyler, *Krit. Zeit.* 10, 32); in barley fat (Stellwaag, *Zeitschr. f. d. g. Brauwes.* 1886, 176; *Chem. Zt.*, *Chem. Repert.* 10, No. 23); in the fat of meadow hay and of oat straw (König, *Landw. Versuchstationen*, 17, 3, 11); in colchicum seeds (Paschkis, *H.* 8, 356); in the oil of the seeds of Chaulmoogra (*Gynocardia odorata*, Roxb.), of Jéquirity (*Abrus precatorius* Lam.), and in the fat of the leaves of *Erythroxylum hyperificifolium* Lam. (Heckel a. Schlagdenhauffen, *C. R.* 102, 1037); probably also in the animal body, possibly together with cholesterin, as may be deduced from older observations (Gmelin, *Handb.* 4, 2092).

Preparation.—(*a*) From peas (Beneke, *loc. cit.*).

(*b*) From calabar beans. These are extracted with petroleum ether. When this is evaporated, a fatty oil is left, out of which phytosterin crystallises. It is separated from the oil by pressure, purified by dissolving in ether with bone black, and recrystallised from alcohol (Hesse, *A.* 192, 176).

(*c*) From beans. The powdered beans are extracted with alcohol, the alcohol distilled, and the residue extracted with ether. This extract is saponified with 25 p.c. NaOH, and the layer of fat separated from the deep-coloured mother liquor. The fat, purified from glycerin, is then extracted with ether, and the phytosterin obtained from this ether extract (Jacobsen, *Inaug. Dissert.* Königsberg in Preussen, 1887).

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[1] It is possible that in some of the cases here mentioned a cholesterin other than phytosterin is present.

(*d*) From the powdered seeds and shoots of the yellow lupine (Schulze a. Barbieri, *J. pr.* [2] 25, 159). The finely powdered seeds and shoots are extracted with ether, the extract distilled, and the residue boiled for several hours with alcoholic potash, using a reflux condenser. The solution thus obtained is evaporated, the residue rubbed up with water and shaken with ether several times. The ether is then distilled off, and the residue dissolved in the least possible quantity of hot alcohol. On cooling, the phytosterin crystallises out. It may then be purified by conversion into the benzoate, re-saponification of this with alcoholic potash, and re-crystallisation from alcohol.

(*e*) Reinitzer recommends the following method for the separation of cholesterin from fats (*M.* 7, 597). The juice—*e.g.* of carrots—is ppd. with $PbAc_2$, the pp. dried, and—together with the pressed vegetable - extracted by carbon bisulphide. The residue after distillation of the bisulphide is saponified with alcoholic potash, the alcohol evaporated, the mass taken up with water and ppd. by $BaCl_2$, and the washed and vacuum-dried pp. extracted by acetone.

Properties.—Glittering plates of $C_{26}H_{44}Oaq$ (from alcohol), silky needles of $C_{26}H_{44}O$ (from chloroform, ether, and petroleum ether). Insol. water or KOHAq, v. sol. hot alcohol, ether, and chloroform. A mixture of phytosterin (from lupines) and cholesterin crystallises from alcohol in a mass of small needles, *i.e.* in a form different from that of either separately.

Reactions.—(*a*) The $CHCl_3$ and H_2SO_4 test gives exactly the same results as with cholesterin and quebrachol (Hesse, *A.* 211, 283).

(*b*) Cautiously evaporated with HCl and Fe_2Cl_6, it gives a violet colour like ordinary cholesterin.

Acetyl derivative $C_{26}H_{43}O(C_2H_3O)$ or $C_{25}H_{41}O(C_2H_3O)$. [120°, Hesse]. [126°, 120°, 118°, and 125° uncor., Jacobsen]. Glancing plates (from alcohol) (Hesse). Resembles in its properties the acetates of cupreol and quebrachol (H.). Prismatic needles (from alcohol) (Jacobsen). Sl. sol. alcohol, v. sol. ether and chloroform.

Benzoyl derivative [145·5°, 147°, 146°, and 145° uncor., Jacobsen]. Thin glancing rectangular plates (from ether), sl. sol. alcohol, m. sol. ether and chloroform. Gives the colour reactions with $CHCl_3$ and H_2SO_4 and with Fe_2Cl_6, but not with HNO_3 and NH_3 (Jacobsen).

Hydrocarotin $C_{26}H_{44}Oaq$? [136·5°] $[a]_D$ (in $CHCl_3$) $-35°$ (Arnaud, *C. R.* 102, 1319; also 100, 751). [138·2°]. $[a]_D$ (in $CHCl_3$) $-37·4$ (Reinitzer, *M.* 7, 579). This substance is probably phytosterin, although Reinitzer considers that it more nearly resembles Liebermann's cholestol (oxyquinoterpene) $C_{30}H_{48}O_2$? [139°], which latter, in its turn, Hesse looks on as being probably almost pure cinchol.

Occurrence and preparation.—In and from carrots.

Properties. Plates (containing aq) (from alcohol), anhydrous needles (from the other solvents). Insol. water, sl. sol. cold, v. sol. hot alcohol, ether, chloroform, &c. Fröhde (*J. pr.* 102, 424) declared hydrocarotin to be cholesterin, which Husemann repudiated. Arnaud, however, finds that Husemann's hydrocarotin (*A.* 117, 200) is phytosterin mixed with some carotene.

Reactions.—Gives the cholesterin reactions with

(*a*) $CHCl_3$ and H_2SO_4

(*b*) HNO_3 and NH_3

(*c*) HCl and Fe_2Cl_6

(*d*) Liebermann's with $(Ac)_2O$ and H_2SO_4 (*B.* 18, 1803).

Acetyl derivatives. [128·2°]. Colourless crystalline scales (from ether-alcohol). Sl. sol. hot alcohol.

Benzoyl derivative. [145°]. Dimetric glancing tables, when slowly crystallised from ether. V. sol. ether. (*Cf.* phytosterin.)

Para-cholesterin $C_{26}H_{44}Oaq$. [134°–134·5° uncor., R. a. R.]. $[a]_D$ (in $CHCl_3$) $-28·88$ and $-27·24$ for different strengths (R. a. R.).

Occurrence.—In the protoplasm of *Ethalium septicum.*

Preparation.—*Ethalium septicum* is digested with alcohol and the whole mass evaporated to dryness and extracted with ether. From this the *p*-cholesterin crystallises out, and is purified by crystallisation from hot alcohol, the cholesterin which is also present remaining in the alcoholic mother liquor (Reinke a. Rodewald, *A.* 207, 229).

Properties. Plates (containing aq) (from alcohol), silky glancing needles (from ether and chloroform). V. sol. hot alcohol, ether, and chloroform, m. sol. cold alcohol. Gives up its water over H_2SO_4. In general properties it agrees with cholesterin, iso-cholesterin, and Beneke's cholesterin from peas, in chemical properties it resembles Hesse's phytosterin.

Reactions.—The $CHCl_3$ and H_2SO_4 test gives much the same colouration as Schulze's iso-cholesterin. At first both the chloroform and sulphuric acid layers are coloured yellowish-brown, the latter with green fluorescence. On prolonged standing the chloroform becomes blue and then violet, while the acid becomes a deeper brown and the fluorescence increases (R. a. R.).

Benzoyl derivative. [127°–128° uncor.]. Thin glancing rectangular plates (from ether). V. sol. ether and chloroform, m. sol. hot, sl. sol. cold, alcohol (R. a. R.).

Caulosterin $C_{26}H_{44}Oaq$. [158°-159°]. $[a]_D$ (in chloroform) $-49·6°$.

Occurrence and preparation.—In the root and growing parts (radicles) of the shoots of the yellow lupine, 'lupinus luteus,' from which it is extracted in the same way as the phytosterin from the seeds (Schulze a. Barbieri, *J. pr.* [2] 25, 159].

Reaction.—*a.* With $CHCl_3$ and H_2SO_4 it behaves in the same way as cholesterin and phytosterin.

Benzoyl derivative.— Thin glancing plates (from ether).

It will be seen from the foregoing description of the cholesterins that much investigation is still required to determine whether they are homologues or isomerides.

1. The various animal cholesterins (from biliary calculi, brains, &c.) have hitherto been considered to be one and the same substance, since preparations from many different sources have been found to possess the same melting-point, and also because of the homogeneity of the benzoic ether (Schulze a. Barbieri); but the point still requires further proof (Reinitzer, *M.* 9). It is not impossible that different cholesterins should occur in different animal organs, just as different varieties were found by Schulze and Barbieri in different parts of the yellow lupine (*cf.* Hesse, *A.* 192). For the probable relation of the cholesterins to the terpenes and camphors *v.* Walitzky (*B.* 9, 1310), Latschinoff (*B.* 12, 1518), Liebermann (*B.* 17, 871; 18, 1803), and Weyl (*Archiv f. Anat. u. Physiol.* 1, 182, *B.* 19, *Ref.* 618). The analogy of cholesterin to camphor is confirmed by the absence of any action when it is treated with hydroxylamine (Rayman, *Bl.* 47).

2. Iso-cholesterin is apparently a simple substance.

3. Para-cholesterin differs little from phytosterin, excepting in specific rotatory power, and requires to be further examined.

4. With regard to vegetable cholesterins, Hoppe-Seyler (*Handb. d. physiol. u. pathol. Chem. Analyse*, 4te Aufl. *p.* 110) surmised that cholesterin was probably a constant constituent of meristematic plant cells. Since they are so widely distributed among plants the cholesterins, according to Schulze and Barbieri, are to be looked upon as invariable constituents of the protoplasm. These last-named authors found cholesterins in very considerable quantity in the etiolated shoots, but only in very small quantity in the green plants of the yellow lupine, and hence they concluded that vegetable cholesterins, especially caulosterin, are decomposition products of albuminous compounds in the life process of the cells, a point already suggested by Hoppe-Seyler (*Handb.* 1, 81). Hesse considers that, because normal cholesterin possesses a stronger rotatory power than phytosterin, the former compound must be the next homologue to $C_{26}H_{44}O$ *i.e.* $C_{25}H_{42}O$, the formula proposed by Walitzky, and also at one time by Berthelot (Gmelin, *Handb. d. Org. Chem.* 4, 2093), although the latter returned later on to the one usually accepted, viz. $C_{26}H_{44}O$; Reinke and Rodewald, however, think this insufficient to overthrow the theory of the isomerism of the cholesterins. Cupreol, cinchol, and quebrachol (all of them $C_{20}H_{34}O,H_2O$), and also Liebermann's cholestol (which is believed by Hesse to be nearly pure cinchol), all belong to this class of cholesterins. Reinitzer is of opinion that cynanocerin, cynanchin, echicerin, and echitine (Hesse, *A.* 192, 182), aspidol (Daccomo, *Centralbl.* 87, 1357), ambrain, castorin, &c., must also be included, and that the cholesterins will ultimately be found to be divisible into two homologous groups, dextro- and lævo-rotatory. For the latest discussion on this point, *v.* Reinitzer (*M.* 9). G. M.

CHOLESTROPHANE *v.* *Di-methyl*-PARABANIC ACID.

CHOLIC ACID $C_{24}H_{40}O_5$ *i.e.* $C_{20}H_{31}(CH.OH)(CH_2.OH)_2CO_2H$ (?) *Cholalic acid.* [195°]. S. (of anhydrous crystals) 133 at 100°; ·025 at 15°.

Formation.—By the hydrolytic action of alkalis on glycocholic and taurocholic acids, which occur in the bile (Demarçay, *A. Ch.* [2] 67, 177; Theyer a. Schlösser, *A.* 48, 77; 50, 235; Strecker, *A.* 65, 9; 67, 1; 70, 161, 166).

Preparation.—Glycocholic acid (50 grms.) is boiled for 16 hours with water (6 litres) and baryta (200 grms.). The liquid is filtered hot and, when cold, HCl added. A sandy pp. of cholic acid falls. Crystallised from alcohol. The yield is 80 p.c. (Hartmann, *J. pr.* [2] 19, 307; *cf.* Tappeiner, *A.* 194, 213).

Properties.—Crystallises from hot water in anhydrous microscopic crystals, from cold solutions, *e.g.* very dilute acetic acid, in trimetric tables (containing aq). The acid combines with methyl-, ethyl-, propyl-, and ethylene-alcohols and with mustard oils, but not with acetone. The hydrated and anhydrous acid and its various alcoholates all crystallise in the trimetric system, the axis-ratio *a:c* remains constant whilst *b:c* varies in the different alcoholates. Gives a blood-red colour with cane sugar and H_2SO_4 (Pettenkofer's test, *v.* BILE).

Reactions.—1. By gentle *oxidation* with acetic acid and CrO_3 it yields dehydrocholic acid $C_{24}H_{34}O_5$, probably $C_{20}H_{31}(CO)(CHO)_2CO_2H$; by more vigorous oxidation with $K_2Cr_2O_7$ and H_2SO_4, bilianic acid $C_{24}H_{34}O_8$ is formed (but no cholanic acid) (*cf.* Destrem, *C. R.* 87, 880; Clève, *C. R.* 91, 1073).—2. By *putrefactive fermentation* it is reduced to desoxycholic acid $C_{24}H_{40}O_4$. The latter acid probably accompanies cholic and choleic acids in saponified ox-gall.—3. Combines with *iodine* and HI or other metallic iodides to form unstable blue compounds $(A'H)_4MI_5$ which greatly resemble iodide of starch in properties.—$(A'H)_4HI_5\,x$aq: formed by adding iodine and HI to an alcoholic solution of cholic acid.—$(A'H)_4KI_5\,x$aq: formed by adding iodine and KI to an alcoholic solution of cholic acid. Small bronzy needles, which suspended in water form an indigo-blue liquid. Readily decomposed into its constituents by heat, great dilution with water, alkalis, &c.—$(A'H)_4BaI_{10}\,x$aq: like the preceding compounds (Mylius, *B.* 20, 683).

Mono-acetyl derivative $C_{24}H_{39}(OAc)O_4$: formed by passing HCl gas through an acetic acid solution of cholic acid. Amorphous powder. V. e. sol. alcohol, ether, benzene, &c.

Di-acetyl derivative $C_{24}H_{38}(OAc)_2O_3$: formed by allowing cholic acid to stand with cold acetic anhydride till it dissolves. White granular crystalline powder. V. sol. alcohol, ether, benzene, &c., insol. water. Bitter taste. Its Ba salt is insol. water (Latschinoff, *Bl.* [2] 33, 297; *B.* 18, 3039; 20, 1043; Mylius, *B.* 19, 369, 2000; 20, 1968). Schotten (*H.* 11, 268) denies the existence of acetyl derivatives of cholic acid.

Amide $C_{24}H_{39}O_4.NH_2$. Formed by heating the acid with alcoholic NH_3 at 250°. Small crystals (containing 3aq). Sl. sol. water. The hydrated compound melts at [125°–130°]. The anhydrous compound melts slowly from [130°–140°], again solidifies at about 180° to a colourless crystalline mass, which again melts at [c. 228°]; if this crystalline mass is crystallised from alcohol, nothing is obtained but the ordinary amide.

Di-methyl-amide $C_{24}H_{39}O_4.NMe_2$. [171°]. Formed by heating the acid with aqueous dimethylamine at 250°.

Anhydrides.—By heating cholic acid under various conditions mixtures of various anhydrides have been obtained, none of which have been isolated in a pure state (Mylius, *B.* 20, 1968).

Ethyl ether $C_{24}H_{39}EtO_5$. [147°].

Preparation.—Cholic acid (20 pts.) is dissolved in dilute (90 p.c.) alcohol (140 pts.) and the solution saturated, in the cold, with dry HCl. An equal volume of alcohol is at once added and every 100 c.c. of the liquid poured in a thin stream into a litre of water. After a few days, needles of the ether appear (Tappeiner; Hartmann).

Dehydrocholic acid $C_{24}H_{34}O_5$ probably $C_{20}H_{31}(CO)(CHO)_2CO_2H$. [232°] (M.). [228° uncor.] (L.). Formed by slowly adding a 10 p.c. solution of CrO_3 (9 pts.) in acetic acid, to a 10 p.c. solution of cholic acid (10 pts.) in acetic acid. Anhydrous needles. By further oxidation with $K_2Cr_2O_7$ and H_2SO_4 it is converted into bilianic acid $C_{24}H_{34}O_8$ *i.e.* $C_{19}H_{31}(CO)_2(CO_2H)_3$. It does not give Pettenkofer's bile reaction.

Tri-oxim $C_{24}H_{34}(NOH)_3O_2$: formed by the action of a cold solution of hydroxylamine upon sodium dehydrocholate. Colourless microscopic tables. Sl. sol. hot alcohol, nearly insol. water and ether. Stable in alkaline solution, but resolved into its components by acids (Latschinoff, *B.* 18, 3045; Mylius, *B.* 19, 2005; 20, 1979).

Phenyl-mercaptide $C_{24}H_{34}O_4(SC_6H_5)_2$: [c. 220°]; colourless glistening needles; sl. sol. water. Formed by passing HCl through a cold solution of the acid in phenyl-mercaptan. The sodium salt forms fine needles, insol. water.

Phenyl-mercaptide-phenyl-hydrazide $C_{23}H_{33}(SC_6H_5)_2(N_2HC_6H_5)_2CO_2H$: separates in colourless needles on warming an acetic acid solution of the phenyl-mercaptide with phenylhydrazine (Mylius, *B.* 20, 1979).

Desoxy-cholic acid (probably identical with the so-called '*hydrated choleic acid*' of Latschinoff) $C_{24}H_{40}O_4$ (M.) or $C_{25}H_{42}O_4$ 1½aq (L.). [135°–140°] (L.); [160°–170°] (M.). Large dimetric crystals, $a{:}a{:}c = 1{:}1{:}2{\cdot}4828$ (L.). White needles, v. sol. alcohol, sl. sol. acetic acid (M.). Occurs, together with cholic and choleic acids, in saponified ox-gall (L.). Formed by putrefactive fermentation of cholic acid (M.). According to L. it is formed in small quantity by boiling choleic acid with acetic acid, but M. was unable to effect this conversion. By gentle oxidation with CrO_3 and acetic acid it is converted into dehydrocholeic acid; by more vigorous oxidation with $K_2Cr_2O_7$ and H_2SO_4 into cholanic acid (L.) (Latschinoff, *B.* 18, 3041; 20, 1043; Mylius, *B.* 19, 373; 20, 1968).

The observations marked (L.) refer to Latschinoff's hydrated choleïc acid, those marked (M.) relate to the desoxycholic acid of Mylius.

CHOLINE *v.* Neurine.

CHOLOÏDANIC ACID $C_{25}H_{38}O_{11}$ *i.e.* $C_{20}H_{33}O(CO_2H)_5$ (?). *Cholecamphoric acid.* S. ·015 at 18°; ·18 at 100°. $[\alpha]_D$ 57° 56′. Formed, together with pseudo-choloïdanic acid, by boiling cholanic acid (1 g.) with HNO_3 (30 c.c. of S.G. 1·28) for several hours. Formed also by the action of HNO_3 on bile (Theyer a. Schlösser, *A.* 50, 243) or cholic acid (Redtenbacher, *A.* 57, 145; Tappeiner, *A.* 194, 239; Clève, *Bl.* [2] 38, 135).

Salts.—A^vAg_5 4aq: gelatinous pp.—$A^v_2Pb_5$: amorphous pp.—$A^v_2Ba_5$ 20aq: thick prismatic crystals, S. (at 18°) about 20 (Latschinoff, *B.* 18, 1052; 19, 1521).

Pseudo-choloïdanic acid $C_{50}H_{71}O_{21}$(?). Formed, together with choloïdanic acid, by boiling cholanic acid (1 g.) with HNO_3 (30 c.c. of S.G. 1·28) for several hours. Microscopic needles.

Salts.—$A^{viii}H_4Ba_2$ 20aq: flat needles.—$A^{viii}Ag_8$: amorphous pp.

Ethyl derivative $C_{50}H_{70}(C_2H_5)_4O_{21}$: [247°]. Obtained by the action of EtI upon the lead salt. Needles. V. sol. alcohol, less in ether.—$C_{50}H_{66}Et_4O_{21}Ba_2$ 2aq: prisms.

Methyl derivative ×$C_{50}H_{70}(CH_3)_4O_{21}$: [194°–196°]; needles.

Neutral methyl ether $C_{50}H_{66}(CH_3)_4O_{21}$: [128°]. Obtained by the action of ethyl iodide upon the silver salt. Flat needles (from alcohol) (Latschinoff, *B.* 19, 1521; *cf.* Clève, *Bl.* [2] 38, 135).

CHONDRIN *v.* Proteïds, *appendix C.*

CHROMATES, *Salts of Chromic Acid*; *v* Chromium, acids of, p. 154.

CHROME ALUM $Cr_2 3SO_4.K_2[or (NH_4)_2]SO_4.24H_2O$ *v.* Alums, also *Sulphates of Chromium* under Sulphates.

CHROMIC ACID H_2CrO_4; *v.* Chromium, acids of, p. 154.

CHROMIC ANHYDRIDE CrO_3; *v.* Chromium, oxides of, p. 164.

CHROMITES, Salts of the form $MO.Cr_2O_3$; *v.* Chromium, acids of, p. 158.

CHROMIUM Cr. At. w. 52·45. Mol. w. unknown. [Above M. P. of Pt which is about 2500°] (Deville, *A.Ch.* [3] 46, 182). S.G. 6·5–6·8 (Wöhler, *A.* 111, 230; Loughlin, *Am. S.* [2] 45, 131; Rammelsberg, *Handbuch d. krystallog. u. physikal. Chemie*, part 1 [1881]). S.H. (22°–50°) ·0998 (uncertain) (Kopp, *T.* 155, 71). S.V.S. about 7·8.

Occurrence.—Never free: chiefly as oxide in combination with FeO as *chrome-ironstone*, $FeO.Cr_2O_3$, with Cr_2O_3 more or less replaced by Fe_2O_3 and Al_2O_3, and FeO by MgO. Also as basic chromate of lead, as chromic oxide, &c. The ores of Cr are not very widely distributed. Chromium was discovered by Vauquelin in 1797; the name was given (χρῶμα) because of the number of compounds of different colours obtained from the metal.

Preparation.—Chrome ironstone is separated from gangue, finely powdered, washed, mixed with CaO and KHO, dried at 150°, and heated to bright redness in contact with air, the mass being constantly stirred; after cooling, the K_2CrO_4 formed is dissolved out in a little warm H_2O, enough conc. H_2SO_4 to convert all the K_2CrO_4 into $K_2Cr_2O_7$ is added, and the $K_2Cr_2O_7$ which separates is re-crystallised from hot H_2O. The $K_2Cr_2O_7$ is heated with S, or starch, or NH_4Cl, and the product washed with H_2O, in which the Cr_2O_3 formed remains undissolved (*v.* Chromic oxide, p. 164). Cr_2O_3 is then mixed with rather less charcoal than is theoretically required for complete reduction, and heated to a very high temperature in a lime crucible. Or, Cr_2O_3 is mixed with charcoal, and heated in Cl whereby $CrCl_3$ (*q.v.*) is obtained; the $CrCl_3$ is then heated to bright redness, and H carrying with it Na vapour is passed over it; monometric crystals of Cr are thus obtained (Fremy, *C. R.* 44, 632). Wöhler (*A.* 111, 230) mixes 1 part violet $CrCl_3$ with 2 parts of a fused and powdered mixture of 7 parts NaCl and 9 parts KCl, presses the mixture firmly into a crucible, and places 2 parts granulated Zn over it, and more NaCl and KCl over this again; he gradually heats until the mass is melted. As soon as the Zn boils, and the flame of burning Zn is seen on removing the crucible, the temperature is decreased, and the mass is kept just melted for 10 minutes. The whole is then allowed to cool, the crucible being shaken once or twice; the crucible is broken, the zinc regulus dissolved in dilute HNO_3Aq, the metallic Cr then boiled once with HNO_3Aq, washed, and dried. Zettnow prepares $CrCl_3$ solution by reducing $K_2Cr_2O_7$ in HClAq by C_2H_6O, adds KCl, evaporates to dryness, and reduces by Zn as already described (*P.* 143, 477). According to Bunsen (*P.* 91, 619) Cr may be obtained in lustrous plates by electrolysing an acid solution of $CrCl_2$ containing $CrCl_3$. Vincent (*P. M.* [4] 24, 328) and Roussin (*J. Ph.* [4] 3, 413) form an amalgam of Cr, by acting on solution of a chromic salt by Na amalgam, and heat this in H or vapour of rock-oil.

Properties.—Descriptions of properties of Cr vary considerably. The metal obtained by reducing $CrCl_3$ by Na vapour, or by reducing Cr_2O_3 by C, is described (Fremy, *C. R.* 44, 632) as unchanged by heating in air, in *aqua regia* or HFAq, or by fusing with KOH or KNO_3. The metal obtained by electrolysis (Bunsen, *P.* 91, 619), or by reducing $CrCl_3$ by Zn (Wöhler, *A.* 111, 230), is oxidised by molten KNO_3 or $KClO_3$, and is dissolved in hot dilute HClAq or H_2SO_4Aq. Berzelius (*A.* 49, 247) supposed that Cr existed in two distinct forms. The metal insoluble in *aqua regia* probably contained Si derived from the vessels. According to Bunsen and Wöhler, Cr is a greyish-white powder, consisting of small, lustrous, very hard, brittle, rhombohedral crystals (dimetric octahedra, Bolley, *C. J.* 13, 333); only superficially oxidised, unless in very fine powder, by heating in air; slowly oxidised by heating to redness in steam; burns brightly when heated in an alcohol flame fed with O; oxidised by molten $KClO_3$ or KNO_3, but not by molten Na_2CO_3; dilute HClAq, or hot dilute H_2SO_4Aq, dissolves it readily with evolution of H; scarcely acted on by hot conc. HNO_3Aq; burns in Cl gas forming violet $CrCl_3$. Cr is less fusible than Pt (Deville, *A. Ch.* [3] 46, 182). It is not magnetic (Wöhler, *A.* 111, 230); slightly magnetic (Faraday).

The atomic weight of Cr has been determined (1) by analysing and determining V.D. of CrO_2Cl_2 and $CrCl_3$; (2) by measuring the S.H. of Cr; (3) by analyses, and comparison with other analogous compounds, of $CrCl_2$ (Péligot, *A. Ch.* [3] 12, 530); Ag_2CrO_4 and $Ag_2Cr_2O_7$ (Berlin, *A.* 56, 207); $Cr_2(NH_4)_2(SO_4)_4.24H_2O$ (Moberg, *J. pr.* 43, 114); $CrCl_3$ (Siewert, *J.* 1861. 241); by synthesis of $BaCrO_4$ from $BaCl_2$ (Wildenstein, *J. pr.* 59, 27); by oxidising $FeCl_2$Aq by $K_2Cr_2O_7$ and by $KClO_3$, and by oxidising As_4O_6Aq by $K_2Cr_2O_7$ (Kessler, *P.* 95, 210); (4) by comparing chromates with isomorphous manganates and tellurates. The atom of Cr is trivalent in the gaseous molecule $CrCl_3$ (Scott, *Pr. E.* 14, 410) (*v.* CHROMIUM HEXAFLUORIDE, under CHROMIUM, FLUORIDES OF, p. 162).

Chromium is both metallic and non-metallic; Cr replaces the H of most acids forming two series of salts, the simplest formulæ for which are CrX_2 and CrX_3, respectively, where $X = Cl_2$ &c., NO_3 &c., $\frac{SO_4}{2}$ &c., $\frac{PO_4}{3}$ &c.; the chromous salts, CrX_2, are very unstable, and are easily oxidised to chromic salts, CrX_3. Many basic chromic salts are known. The oxide Cr_2O_3 is basic towards acids, and at the same time exhibits feebly acidic properties; CrO_2 seems to be a neutral oxide and not to form salts either by the action of acids or alkalis; CrO_3 is distinctly an anhydride. CrO_3Aq behaves as a dibasic acid, forming a series of salts M_2CrO_4, the acid H_2CrO_4 has also been obtained. Although no salts of the form $MHCrO_4$ are known as definite solids, yet the thermal reactions of CrO_3Aq point to the formation of these salts; thus (*Th.* 1, 254)

n	[CrO^3Aq, n NaOHAq]
1	13,134
2	24,720
4	25,164.

By the action of acids on M_2CrO_4, dichromates, $M_2Cr_2O_7$, are formed: a few tri- and tetra- chromates, $M_2Cr_3O_{10}$ and $M_2Cr_4O_{13}$, are known. CrO_3 also reacts with strong acids to form chromic salts and O; it combines directly with a few anhydrides, *e.g.* with SO_3. Chromic oxide, Cr_2O_3, reacts towards acids as a salt-forming oxide, but at the same time it combines with some of the more positive metallic oxides, *e.g.* with CaO, MnO, ZnO. Several hydroxides of Cr, or perhaps rather hydrated oxides, are known, derived from the oxide Cr_2O_3, and the lower oxide CrO which has not itself been obtained free from Cr_2O_3; these hydrates are salt-forming in their reactions with acids. The pps. produced by adding KOHAq or NaOHAq to solutions of chromic salts always contain potash or soda which cannot be removed by washing with hot water. Cr_2S_3 exhibits slight salt-forming properties in its reactions towards sulphides of more positive metals; no hydrosulphide of Cr is known. Chromium is closely related to Mo, W, and U; less closely to S, Se, and Te; it also shows distinct relations to Al, Mn, and Fe (*v.* CHROMITES; CHROMIUM GROUP OF ELEMENTS; also CHROMIUM, SALTS OF; CHROMATES; and the arts. on HYDROXIDES, OXIDES, CHLORIDES, &c. OF CHROMIUM).

Reactions.—1. Decomposes *steam* at bright red heat.—2. Dissolves in *hydrochloric* and *sulphuric acids*, forming salts and H.—3. Oxidised by molten *potassium nitrate* or *chlorate.*—4. Burns when heated in *chlorine*, forming $CrCl_3$. 5. Is oxidised by strongly heating in *oxygen.*—6. Forms CrN by heating in *nitrogen*, and Cr_2S_3 by heating with *sulphur.*

Combinations.—Most of the compounds of Cr are obtained directly or indirectly from the oxides. The metal combines directly with Cl, N, O, and S. Compounds of Cr with each of the non-metals, except H, B, Si, and Te, are known; alloys with Al, Fe, and Hg, have been prepared (*v.* **the various binary compounds of Cr, also** CHROMIUM, ALLOYS OF).

Estimation.—Chromium may be estimated in the form of oxide Cr_2O_3, after ppn. by NH_4Aq from a warm solution. Chromates are usually estimated as $BaCrO_4$, or they may be ppd. by $HgNO_3Aq$, and the Hg_2CrO_4 heated until only Cr_2O_3 remains; or the chromate may be reduced, by alcohol, to a chromic salt, and the Cr determined by ppn. with NH_3Aq &c. Cr may be separated from many heavy metals by ppg. these metals as sulphides, by H_2S; Ba and Sr are best separated by ppn. with H_2SO_4Aq; separation from Ca, Mg, and Fe, is effected by ppg. $Cr_2O_3.xH_2O$ by NH_3Aq, collecting, drying, and fusing with KNO_3 and K_2CO_3 until all the Cr exists as K_2CrO_4, dissolving in water and ppg. as Hg_2CrO_4 or $BaCrO_4$. If alumina is present, it is ppd. from the solution containing K_2CrO_4 by digesting with ammonium carbonate. $Cr_2O_3xH_2O$ is ppd. by digesting solutions of chromic salts with excess of $BaCO_3$; under the same conditions salts of Ni, Co, Mn, and Zn, are not ppd.

Chromium, acids of, and their salts (comp. arts. ACIDS; ACIDS, BASICITY OF; HYDROXIDES) Chromic acid H_2CrO_4 is said to have been obtained in definite form, by the action of H_2O on the anhydride CrO_3 (*v. infra*, CHROMIC ACID). This acid forms a series of chromates, M_2CrO_4, isomorphous with M_2SO_4. H_2CrO_4Aq reacts as a dibasic acid (*v. infra*, CHROMIC ACID); no salts of the form $MHCrO_4$, but only the salts M_2CrO_4, have been obtained by neutralising the acid by alkalis; when acids react with chromates of monovalent metals M_2CrO_4, two formula-weights of the chromate usually react with one formula-weight of a dibasic acid (*e.g.* H_2SO_4), half of M is removed, and a *dichromate*, $M_2Cr_2O_7$—similar to the disulphates $M_2S_2O_7$—is produced. Several *trichromates* $M_2Cr_3O_{10}$, and *tetrachromates* $M_2Cr_4O_{13}$, are also known; these salts are probably best regarded as derived from $M_2Cr_2O_7$ and M_2CrO_4, and from $2M_2Cr_2O_7$, respectively, by the removal of half the total M and condensation of the residues. The following formulæ express this view of the constitution of the di-, tri-, and tetra-, chromates:

(1) *Chromic acid*, $CrO_2(OH)_2$;
(2) *Chromates*, $CrO_2(OM)_2$;
(3) *Dichromates*, $OM.CrO_2.O.CrO_2.OM$;
(4) *Trichromates*, $OM.CrO_2.O.CrO_2.O.CrO_2.OM$;
(5) *Tetrachromates*,
$OM.CrO_2.O.CrO_2.O.CrO_2.O.CrO_2.OM$.

These various series of salts may also be regarded as direct compounds of metallic oxide with CrO_3 ($M_2O.CrO_3$; $M_2O.2CrO_3$; $M_2O.3CrO_3$; $M_2O.4CrO_3$). Besides these salts, several basic chromates are known (*v. infra*). Chromic acid, H_2CrO_4, being dibasic, and forming M_2CrO_4 analogous with M_2SO_4, is probably a dihydroxyl acid, $CrO_2(OH)_2$. If this is so we should expect that each OH would be replaceable by Cl; the first compound thus produced, $CrO_2.Cl.OH$, ought to be a monobasic acid (analogous with $SO_2.Cl.OH$); this compound is not itself known, but several salts derived from it have been prepared, *e.g.* $CrO_2.Cl.OK$ (*v. infra*, under **Chromates**). *Fluo-*, *bromo-*, and *iodo-*, *chromates*, $CrO_2.X.OM$ (where X = F, &c., and M = alkali metal), are also known. Salts of the hypothetical *amido-chromic acid* ($CrO_2.NH_2.OM$) are known; and it is probable that *nitro-derivatives* of $K_2Cr_2O_7$ and $K_2Cr_3O_{10}$, respectively, have been obtained, viz. $Cr_2O_5.NO_2.OK$ and $Cr_3O_8.NO_2.OK$ (*v. Potassium dichromate*, under **Dichromates**). Cr_2O_3 reacts towards acids as a salt-forming or positive oxide; no acid corresponding to this oxide is known; the oxide is itself insoluble in H_2O. Salts $MO.Cr_2O_3$, where M = Zn, Mn, Fe, &c., have, however, been prepared, by fusing MO and Cr_2O_3 with B_2O_3, &c; these may be regarded as derivatives of the hypothetical chromous acid $H_2Cr_2O_4$ (*v.* **Chromites**, p. 158). The sulphide Cr_2S_3, corresponding to Cr_2O_3, also reacts as a feebly salt forming compound towards more positive sulphides (*v.* CHROMIUM, THIOACID OF, p. 168).

CHROMIC ACID H_2CrO_4. Said to be obtained as small red crystals by adding a little H_2O to excess of pure CrO_3, keeping the solution for some hours at 90°, decanting and cooling to 0° (**Moissan,** *A. Ch.* [6] **5, 568**). **But Miss Field has** shown that the crystals thus obtained are CrO_3; the solution, however, probably contains H_2CrO_4 and $H_2Cr_2O_7$ (*C. J.* **61, 405** [1892]). The thermal values of the reaction between NaOHAq and H_2CrO_4Aq show that this acid is dibasic; salts of the form $MHCrO_4$ appear not to exist as solids; if enough alkali is added to saturate half the H_2CrO_4 in solution, and the liquid is evaporated, the salt $M_2Cr_2O_7$ is obtained probably $2MHCrO_4$ is formed and decomposed to $M_2Cr_2O_7$ and H_2O. If H_2CrO_4Aq is added to solution of M_2CrO_4, $M_2Cr_2O_7$ is obtained on evaporation. The thermal data (*Th.* 1, 255) show (1) the dibasicity of the acid, and (2) the action of excess of acid on the normal salts: the corresponding data for H_2SO_4Aq are given; addition of H_2SO_4Aq to K_2SO_4Aq produces $KHSO_4Aq$:—

n	[*n*NaOHAq, CrO^3Aq]	*m*	[*m*CrO^3Aq, 2NaOHAq]
1	13,134	½	12,582
2	24,720	1	24,720
4	25,164	2	26,268

n	[*n*NaOHAq, SO^3Aq]	*m*	[*m*SO^3Aq, 2NaOHAq]
1	14,754	½	15,689
2	31,378	1	31,378
4	31,368	2	29,508

Chromates. (*Di-, tri-, tetra-, chromates.*) M_2CrO_4 or $M^{II}CrO_4$; also basic and double salts. Chromates are mostly yellow or red; the salts of the alkali metals, and of Ca, Mg, and Sr, are e. sol. water, the others are generally insol. or sl. sol. They are formed by the action of bases on H_2CrO_4Aq; by fusing Cr_2O_3 with alkali in presence of air; or by double decomposition from the alkali salts. Neutral M_2CrO_4Aq (M = alkali metal) goes red on addition of a mineral acid from formation of $M_2Cr_2O_7Aq$, on adding alkali the yellow colour returns. Chromates are easily reduced to Cr_2O_3 or salts of this oxide; *e.g.* boiling HClAq produces $CrCl_3Aq$, and chloride of the metal, H_2SO_4Aq produces Cr_23SO_4Aq. Chromates of the less positive metals give Cr_2O_3 when strongly heated; $M_2Cr_2O_7$ (M = alkali metal) give Cr_2O_3, O, and M_2CrO_4. Insoluble chromates yield alkali chromates by fusion with KOH or NaOH. Heated with NaCl and conc. H_2SO_4, chromates give CrO_2Cl_2. Solutions of chromates have a metallic taste, and are poisonous.

Aluminium chromate. — The basic salt $Al_23CrO_4.2Al_2O_3.21H_2O(=Al_2O_2.CrO_4.7H_2O)$ is a flocculent yellow pp. obtained by adding K_2CrO_4Aq to alum solution, or by evaporating $Al_2O_3.xH_2O$ in CrO_3Aq (Fairrie, *C. J.* 4, 300; Mans, *P.* **11**, 81; Elliot a. Storer, *P. Am. A.* **5**, 192).

Ammonium chromate.—$(NH_4)_2CrO_4$. Citron-yellow needles; e. sol. water; gives off NH_3 in air; on heating leaves Cr_2O_3. Obtained by slowly adding CrO_2Cl_2 to excess of NH_4Aq, and evaporating below 60°; also by $BaCrO_4 + (NH_4)_2SO_4Aq$, and by $CrO_3Aq + NH_3Aq$ (Darly, *A.* **65**, 2041) (*v.* **Di-, Tri-, and Hexa-chromates**).

Barium chromate $BaCrO_4$. Yellow, crystalline powder; obtained by $K_2CrO_4Aq + BaCl_2Aq$; S.G. 3·9; also by fusing 1 pt. K_2CrO_4 with 1 pt. Na_2CrO_4 and 2 pts. $BaCl_2$, and cooling slowly; S.G. 4·6 (Bourgeois, *Bl.* [2] 31, 243). Insol. H_2O; sol. HClAq, or HNO_3Aq, and reppd. by NH_3Aq. Decomposed by alkali carbonates and sulphates (Rose, *P.* 95, 426) (*v.* **Dichromates**).

Beryllium chromate.—Basic salt $BeCrO_4.13BeO.23H_2O$; yellow pp., insol. H_2O (Creuzburg, *D. P. J.* 163, 449).

Bismuth chromates (Löwe, *J. pr.* 67, 288 a. 463; Pearson, *P. M.* [4] 11, 204; Pattison Muir, *C. J.* [2] 15, 12; [2] 16, 24 a. 645). Normal chromate, Bi_23CrO_4, has not been prepared. The following basic salts are known:— $2(Bi_23CrO_4).7Bi_2O_3$, by ppg. $Bi3NO_3$ in smallest excess of HNO_3Aq by K_2CrO_4Aq; $2(Bi_23CrO_4).Bi_2O_3$, by ppg. a more acid solution of $Bi3NO_3$ in HNO_3Aq by K_2CrO_4Aq; $(Bi_23CrO_4).2Bi_2O_3$, by boiling the preceding salt with dilute HNO_3Aq or with alkali; $3(Bi_23CrO_4).Bi_2O_3$, by prolonged heating $2(Bi_23CrO_4).Bi_2O_3$ with dilute HNO_3Aq; $7(Bi_23CrO_4).2Bi_2O_3$, by treating $(Bi_23CrO_4).2Bi_2O_3$ first with conc., then with dilute, HNO_3Aq. These salts are all yellow to red, heavy, crystalline powders; insol. water, and slowly decomposed by hot acids (*v.* also **Dichromates**).

Cadmium chromate.—Basic salt $CdCrO_4.CdO.H_2O$; by reaction of $CdSO_4Aq$ with large excess of K_2CrO_4Aq (Freese, *B.* 2, 476; Sarzeau a. Malaguti, *A. Ch.* [3] 9, 431).

Calcium chromate $CaCrO_4.2H_2O$; by dissolving $CaCO_3$ in CrO_3Aq and evaporating. Yellow prisms; S. (14°) ·41; insoluble in alcohol; loses its H_2O at 200° (Siewert, ***Z. f. d. g. Naturwiss.*** 19, 11) (*v.* **Dichromates**).

Cerium chromate $Ce(CrO_4)_2$; yellow powder, by dissolving $Ce(CrO_3)_2$ in CrO_3Aq and evaporating (Beringer, *A.* 42. 143).

Chromium chromate $(Cr_23CrO_4).2Cr_2O_3$. This name and composition is sometimes assigned to CrO_2 (*v.* CHROMIUM DIOXIDE under CHROMIUM, OXIDES OF, p. 164.)

Cobalt chromates.—Basic cobaltous salt $CoCrO_4.CoO.2H_2O$ (Freese, *B.* 2, 476); $CoCrO_4.2CoO.4H_2O$ (Sarzeau a. Malaguti, *A. Ch.* [3] 9, 431). Clear red-brown pp. by $Co2NO_3Aq + K_2CrO_4Aq$. Cobaltic chromate Co_23CrO_4 is known in combination with NH_3 and NH_4Cl; the salts $(Co_23CrO_4).10NH_3$, $(Co_23CrO_4).12NH_3.5H_2O$, and $(Co_23CrO_4).2NH_3.2NH_4Cl$, are described by Braun (*A.* **125, 153 a. 197**), Gibbs a. Genth (*A.* **104, 150 a. 295**), and Gibbs (*B.* **4, 790**) (*v.* also **CHROMIUM, AMMONIO-SALTS OF**).

Copper chromates.—Basic salts: $CuCrO_4.2CuO.2H_2O$, yellowish-brown pp., by $K_2CrO_4Aq + CuSO_4Aq$, and by $CuSO_4Aq + K_2Cr_2O_7Aq$ and adding enough KOH to produce K_2CrO_4Aq (Freese, *P.* 140, 87; Rosenfeld, *B.* 13, 1469). Loses its H_2O at 260° and takes it up again in moist air. Two salts, $2(CuCrO_4).5CuO.5H_2O$, and $CuCrO_4.6CuO.5H_2O$, are described by Rosenfeld (*l.c.*); obtained by adding $CuSO_4Aq$ to $K_2Cr_2O_7Aq$ with excess of KOHAq. The salt $CuCrO_4.2CuO.2H_2O$ dissolves in NH_3Aq at 0°; dark-green crystals of $2(CuCrO_4)CuO.10NH_3.2H_2O$ separate (Sarzeau a. Malaguti, *A. Ch.* [3] 9, 431; Viefhaus, *J. pr.* 88, 431; Slater, *J. pr.* 60, 247) (*v.* also *Potassium chromate*).

Iron chromate.—Basic ferric salt $(Fe_23CrO_4).2Fe_2O_3$; brown pp. by K_2CrO_4Aq acting on iron-alum solution; decomposed by H_2O to Fe_2O_3 and CrO_3Aq. An acid salt, $Fe_23CrO_4.CrO_3$, is said to be formed by digesting CrO_3Aq with $Fe_2O_6H_6$, and evaporating (Kletzinsky, *D. P. J.* 207, 83; Elliot a. Storer, *P. Am. A.* 5, 192).

Lead chromate $PbCrO_4$. Occurs native as *red-lead ore*, in yellow, translucent, monoclinic prisms, S.G. 5·2 to 6·1. Obtained as yellow pp. by K_2CrO_4Aq or $K_2Cr_2O_7Aq$ acting on neutral solution of a Pb salt; also in crystals by strongly heating K_2CrO_4 with $PbCl_2$, S.G. of crystals 6·12 (Manross, *A.* 82, 348; Drevermann, *A.* 87, 120). S.H. ·09 (Kopp, *A. Suppl.* 3, 1). Insol. in H_2O, sol. in HNO_3Aq or KOHAq; melts without change, but at higher temperature gives O, Cr_2O_3, and a basic salt $(PbCrO_4.PbO)$. Acts as an oxidiser, hence used in organic analysis (*v.* Vohl, *A.* 106, 127).

Basic salt $PbCrO_4.PbO$; red crystals, obtained by throwing $PbCrO_4$ in small quantities into molten KNO_3, cooling somewhat, pouring off still liquid part, and quickly washing residue with H_2O; also by digesting $PbCrO_4$ with cold KOHAq, or with hot K_2CrO_4Aq. Insol. in H_2O; sol. in KOHAq; acids withdraw PbO (Wöhler a. Liebig, *P.* 21, 580). Another basic salt, $2(PbCrO_4).PbO$, occurs native as *Melanochroïte*, and is said to be formed by diffusing K_2CrO_4Aq and $Pb2NO_3Aq$ (Drevermann, *A.* 87, 120). Lead chromates are used as pigments.

Lithium chromate $Li_2CrO_4.H_2O$; red trimetric crystals, easily sol. in H_2O. A double salt, $Li.NH_4.CrO_4.2H_2O$, is obtained by saturating $Li_2Cr_2O_7Aq$ with NH_3Aq (Rammelsberg, *B. B.* 1865. 629) (*v.* **Dichromates**).

Magnesium chromate $MgCrO_4.7H_2O$. Citron-yellow soluble crystals; isomorphous with $MgSO_4.7H_2O$; S.G. 1·66–1·75; by dissolving MgO in CrO_3Aq and evaporating (Kopp, *A.* 42, 100; Grailich, *W. B.* 27, 174).

The double salt $MgCrO_4.NH_4CrO_46H_2O$ crystallises from a solution of its constituents; yellow monoclinic crystals, isomorphous with corresponding double sulphates (Grailich, *l.c.*). *v.* also *Potassium chromate.*

Manganese chromate.—Basic manganous salt; $MnCrO_4.MnO.2H_2O$, brown pp. by reaction of boiling $MnSO_4Aq$ and K_2CrO_4Aq (Fairrie, *C. J.* 4, 300; Freese, *P.* 140, 87; Warington, *P. M.* [3] 21, 380; Reinsch, *P.* 55, 97).

Mercury chromates.—Mercurous chromate Hg_2CrO_4; red crystalline powder; by reaction of

$HgNO_3Aq$ and K_2CrO_4Aq or $K_2Cr_2O_7Aq$ (H. Rose, *P.* 53, 124; Freese, *Z.* [2] 6, 30). Decomposed by heat to Hg, O, and Cr_2O_3 (Darly, *A.* 65, 204; Freese, *P.* 140, 87). By action of alkalis a black basic salt, $Hg_2CrO_4.2Hg_2O$, is obtained (Richter, *B.* 15, 1489).

Mercuric chromate $HgCrO_4$; dark, garnet-red, trimetric prisms; obtained by evaporating equal parts of yellow HgO and CrO_3 in H_2O. Decomposed by H_2O to CrO_3Aq and $HgCrO_4.2HgO$. Decomposed by acids (Geuther, *A.* 106, 247; Millon, *A. Ch.* [3] 18, 365).

The basic salt $HgCrO_4.2HgO$ is a brick-red powder, obtained by boiling HgO with K_2CrO_4Aq, or by reaction of $Hg2NO_3Aq$ and $K_2Cr_2O_7Aq$ (Millon, *A. Ch.* [3] 18, 365; Freese, *Z.* [2] 6, 30).

A double salt $2(HgCrO_4).HgS$ is obtained by digesting freshly ppd. HgS with solution of freshly ppd. HgO in CrO_3Aq, and drying at 30°; easily explodes when rubbed (Palm, *J.* 1862. 221) (*v.* also *Ammonium dichromate*).

Nickel chromate.—Basic salt $NiCrO_4.2NiO.6H_2O$; brown pp. by reaction between $NiSO_4Aq$ and K_2CrO_4Aq. Loses its H_2O above 300° (Freese, *P.* 140, 87). Other basic nickel chromates are described by Schmidt (*A.* 156, 19). A double compound, $NiCrO_4.6NH_3$, is obtained in yellow dichroic crystals by addition of alcohol to a solution of the basic salt in presence of NH_3Aq; the crystals lose NH_3 in the air (Schmidt, *l.c.*).

Potassium chromate K_2CrO_4. S.G. $\frac{4^\circ}{}$ 2·71. S.H. ·189 (Kopp, *A. Suppl.* 3, 1). C.E. (0° 100°) ·01134 (Joule a. Playfair, *C. J.* 1, 121; Schiff, *A.* 107, 64). S. (0°) 58·9; (20°) 62·94; (60°) 71·02; (100°) 79·1: boiling-point of saturated solution = 101·2° (Michel a. Kraft, *A. Ch.* [3] 41, 471; Schiff, *A.* 108, 326; v. Hauer, *J. pr.* 103, 114). Freezing-point of saturated solution = −12·5° (Rüdorff, *P.* 122, 337). S.G. $\frac{19\cdot5^\circ}{}$ 38·44 p.c. solution = 1·3787; 17·09 p.c. solution = 1·1476; 8·54 p.c. solution = 1·0703; 4·27 p.c. solution = 1·0349 (Michel a. Kraft, *A. Ch.* [3] 41, 417; Alluard, *C. R.* 59, 500).

Preparation.—1. By heating 5 parts $K_2Cr_2O_7$ with 4 parts KNO_3 or K_2CO_3 until the whole fuses quietly, dissolving in water, and crystallising.—2. By neutralising $K_2Cr_2O_7Aq$ with K_2CO_3, evaporating and crystallising. 3. By fusing Cr_2O_3 with K_2CO_3 and KNO_3, dissolving in water and crystallising.—4. By fusing chrome-ironstone with K_2CO_3 and CaO_2H_2, lixiviating with H_2O, boiling down, and crystallising.

Properties.—Pale lemon-yellow, double six-sided trimetric pyramids; isomorphous with K_2SO_4. Melts without change. Insol. alcohol. Solution in H_2O is alkaline, with metallic taste, and is poisonous; on evaporation, this solution gives crystals of $K_2Cr_2O_7$, and mother liquor gives crystals of K_2CrO_4.

Reactions.—1. *Acids*, even CO_2Aq, produce $K_2Cr_2O_7$ (Schweitzer, *N. R. P.* 3, 212; Margueritte, *J. pr.* 64, 502; Mohr, *Fr.* 1872. 278).—2. Reduced by H_2S or K_2SAq, with formation of $Cr_2O_3.xH_2O$, and by SO_2Aq with production of Cr_23SO_4Aq.—3. With HCl gas, KCl, H_2O, and $K_2Cr_2O_7$ are formed, and then the $K_2Cr_2O_7$ is reduced to $CrCl_3$ and CrO_2 (Thomas, *C. J.* 33, 371).

Combinations.—1. With various *chromates* to form double salts. $K_2CrO_4.(NH_4)_2CrO_4$ crystallises from conc. $K_2Cr_2O_7Aq$ saturated with NH_3 (Berthier, *A. Ch.* [3] 7, 77; Johnson, *J. pr.* 62, 261). $K_2CrO_4.CaCrO_4.2H_2O$ crystallises from $K_2Cr_2O_7Aq$ neutralised by CaO_2H_2Aq.

$K_2CrO_4.5CaCrO_4$ obtained by slowly evaporating a mixture of $CaCl_2Aq$ and K_2CrO_4Aq (Bahr, *J. pr.* 60, 60; Duncan, *J. pr.* 50, 54; Rammelsberg, *P.* 98, 507). $K_2CrO_4.2CuCrO_4.CuO.2H_2O$, obtained by reaction between cold $CuSO_4Aq$ and K_2CrO_4Aq, or by adding KOHAq to mixture of $K_2Cr_2O_7Aq$ and $CuSO_4Aq$ (Freese, *P.* 140, 87). $K_2CrO_4.Fe_23CrO_4.4H_2O$, by reaction between conc. Fe_2Cl_6Aq and K_2CrO_4Aq, dissolving pp. in HClAq, cooling, and washing rapidly with cold H_2O (Hengson, *B.* 12, 1300 a. 1656). $K_2CrO_4.MgCrO_4.2H_2O$; by evaporating conc. $K_2Cr_2O_7Aq$ after neutralising by MgO or $MgCO_3$ (Hauer, *J. pr.* 80, 222; Schweitzer, *A.* 64, 276). $K_2CrO_4.2ZnCrO_4.2ZnO.3H_2O$; by prolonged action of cold $ZnSO_4Aq$ on excess of K_2CrO_4Aq (Freese, *B.* 2, 476; Prüssen a. Philippona, *A.* 149, 92).—2. With *mercuric chloride* and *cyanide*, to form $K_2CrO_4.2HgCl_2$, and $2K_2CrO_4.3Hg(CN)_2$, respectively (Darly, *A.* 65, 204; Rammelsberg, *A.* 28, 217; 84, 281) (*v.* also **Di-, Tri-, and Tetrachromates**; also **Bromo-, Chloro-, Fluo-, Iodo-, Chromates**).

Rubidium chromate Rb_2CrO_4. Yellow trimetric crystals, isomorphous with K_2CrO_4 and K_2SO_4 (Piccard, *J. pr.* 86, 449; Grandeau, *A. Ch.* [3] 67, 155).

Silver chromate Ag_2CrO_4. Dark-red crystals; by reaction between K_2CrO_4Aq and $AgNO_3Aq$, or by digesting moist Ag_2O with K_2CrO_4Aq. Insol. H_2O; sol. acids, NH_3Aq, and alkali chromates; KOHAq withdraws all CrO_3. Under H_2O is slowly reduced by Zn, Cd, Sn, &c. (Freese, *P.* 140, 87; Fischer, *P.* 8, 488). Combines with NH_3 to form $Ag_2CrO_4.4NH_3$; produced in yellow crystals, isomorphous with corresponding sulphate and selenate, by dissolving Ag_2CrO_4 in hot NH_3Aq and crystallising (Mitscherlich, *P.* 12, 141; Wöhler a. Rantenberg, *A.* 114, 119).

Sodium chromate $Na_2CrO_4.10H_2O$; yellow, deliquescent crystals, isomorphous with $Na_2SO_4.10H_2O$. Prepared similarly to K_2CrO_4 (Johnson, *J. pr.* 62, 261; Kopp, *A.* 42, 100) (*v.* also **Dichromates**).

Thallium chromate Tl_2CrO_4. Yellow pp. obtained by reaction between K_2CrO_4Aq and neutral solution of a thallous salt (Carstanjen, *J. pr.* 102, 65 a. 129; Hebberling, *A.* 134, 11; Strecker, *A.* 135, 207; Crookes, *C. N.* 8, 255) (**v.** also **Di-**, and **Tri-chromates**).

Thorium chromate $Th_2CrO_4.8H_2O$; crystallises by evaporating a solution of Th_2O_3 in CrO_3Aq (Chydenius, *P.* 119, 43).

Zinc chromates.—Various basic salts are obtained by the reactions between $ZnSO_4Aq$ and K_2CrO_4Aq: the most marked seems to be $ZnCrO_4.ZnO.2H_2O$ (Sarzeau a. Malaguti, *A. Ch.* [3] 9, 431; Thomson, *P. M.* 3, 81; Prüssen a. Philippona, *A.* 149, 92). By dissolving this salt in a little NH_3Aq, and adding alcohol, $ZnCrO_4.4NH_3.3H_2O$ is obtained (Sarzeau a. Malaguti, *l.c.*; Bieler, *A.* 151, 223) (*v.* also *Potassium chromate*).

Chromates of In (Meyer, *A.* 150, 137); Mo; Sr; Sn (Leykauf, *J. pr.* 19, 127); U; and Yb (Popp, *A.* 131, 179) seem to exist, but very little is known concerning them, nor have their compositions been satisfactorily determined.

Fluo-, Bromo-, Chloro-, and Iodo-chromates; also **Amido-chromates** (*v. supra* beginning of this art., p. 154). Salts derived from the hypothetical acids, *fluochromic* $CrO_2.F.OH$, *bromochromic* $CrO_2.Br.OH$, &c., and *amidochromic* $CrO_2.NH_2.OH$. These acids are not themselves known.

Potassium fluochromate $CrO_2.F.OK$. Ruby red, semitransparent, crystals; efflorescent in air; melts when heated; acts on glass. Prepared by heating powdered $K_2Cr_2O_7$ in a Pt dish with excess of conc. HFAq (Streng, *A.* 129, 225; Heintze, *J. pr.* [2] 4, 225; Varenne, *C. R.* 89, 358; 91, 389).

Potassium bromochromate $CrO_2.Br.OK$. Dark-brown crystals; gives up Br in an exsiccator; decomposed by H_2O. Obtained by saturating conc. $K_2Cr_2O_7Aq$ with fuming HBrAq, and crystallising from HBrAq (Heintze, *J. pr.* [2] 4, 225).

Potassium chlorochromate $CrO_2.Cl.OK$. Obtained by heating for a short time 3 parts $K_2Cr_2O_7$ with 4 parts conc. HClAq and a little H_2O, and cooling; or by adding CrO_2Cl_2 to KClAq, or to K_2CrO_4Aq slightly acidified with acetic acid:

$$K_2Cr_2O_7 + 2HClAq = 2CrO_2.Cl.OK + H_2OAq;$$
$$CrO_2Cl_2 + KClAq + H_2O = CrO_2.Cl.OK + 2HClAq;$$
$$CrO_2Cl_2 + K_2CrO_4Aq = 2CrO_2.Cl.OK + Aq$$

(Péligot, *A. Ch.* 52, 267; Geuther, *A.* 106, 240). This salt is also produced, along with Cr_2O_3, when violet $CrCl_3$ reacts with molten $K_2Cr_2O_7$ (Geuther, *A.* 118, 68). Large red prisms; S.G. $\underline{4^\circ}$ 2·497; C.E. (0°–100°) ·0159 (Playfair a. Joule, *C. J.* 1, 121). May be crystallised unchanged from H_2O containing a little acid; crystals of $K_2Cr_2O_7$ separate from an aqueous solution. Cl is evolved at 100°. Decomposed by conc. H_2SO_4 with formation of CrO_2Cl_2 and $Cr_3O_6Cl_2$ (*q. v.*); with NO_2 gives NO_2Cl (Heintze, *J. pr.* [2] 4, 211). By reaction with conc. KCNAq, CNCl is formed. By the action of dry NH_3, salt having the composition $K_2Cr_3O_8$ (?$CrO_2.OK.CrO_2.OK.CrO_2$) is formed, along with KCl and NH_4Cl; if the chlorochromate is suspended in $(C_2H_5)_2O$ and NH_3 is passed in, crystals of potassium amidochromate $CrO_2.NH_2.OK$ (*q. v.*) are formed (Heintze, *J pr.* [2] 4, 211).

Chlorochromates of Na—$CrO_2.Cl.ONa.2H_2O$; of NH_4—$CrO_2.Cl.ONH_4$; of Ca, Sr, Ba, Mg, Ni, Co, and Zn—$(CrO_2.Cl.O)_2M.xH_2O$; have also been prepared, by adding CrO_2Cl_2 to fairly conc. solution of the metallic carbonates in CrO_3Aq. When M = Mg, Ni, Co, or Zn, the salts crystallise with $9H_2O$; when M = Ca, with $5H_2O$; when M = Sr, with $4H_2O$; and when M = Ba, with H_2O (Péligot, *A. Ch.* 52, 267; Prætorius, *A.* 201, 1).

Potassium iodochromate $CrO_2.I.OK$. Obtained, as garnet-red, easily decomposed, crystals, by gently heating conc. colourless HIAq with finely powdered $K_2Cr_2O_7$ (Guyot, *C. R.* 73, 46).

Potassium amidochromate $CrO_2.NH_2.OK$. Finely powdered $CrO_2.Cl.OK$ is slowly added to water and ether (free from alcohol), the liquid is simultaneously saturated with NH_3; after standing 24 hours, the ether is poured off, the residue is gently warmed to get rid of adhering ether, and is then treated with water; the liquid is evaporated at a low temperature, and allowed to crystallise. The salt is recrystallised from H_2O, and the crystals are dried at 100°. Garnet-red, unchanged by cold H_2O, or cold NaOHAq; decomposed by H_2O, or NaOHAq, at 100°, giving $CrO_2.OK.ONH_4$, and $CrO_2.OK.ONa$, respectively; decomposed by nitrous acid to $K_2Cr_2O_7$, N, and H_2O. $CrO_2.NH_2.OK$ is changed by dry NH_3 to a dark-brown powder, from which H_2O removes NH_4Cl and leaves a crystalline salt, $Cr_3O_6(OK)_2$: the corresponding NH_4 salt is obtained by acting on CrO_2Cl_2 dissolved in $CHCl_3$ with NH_3, and reacting with H_2O (Heintze, *J. pr.* [2] 4, 214).

Dichromates $M_2Cr_2O_7$ **and** MCr_2O_7. Most of these salts are soluble in water; many of them are decomposed by water. The greater number are salts of monovalent metals. They are obtained by the action of acids on M_2CrO_4.

Ammonium dichromate $(NH_4)_2Cr_2O_7$. Orange coloured, monoclinic, crystals; S.G. 2·367; decomposed by heat to Cr_2O_3, H_2O, and N. Prepared by neutralising CrO_3Aq with NH_3Aq, adding an equal quantity of CrO_3Aq, and evaporating (Richmond a. Abel, *C. J.* 3, 199; Siewert, *Z. f. d. g. Naturwiss.* 19, 11; Schabus, *P.* 116, 420; Weiss, *Sitz. W.* 37, 373; Rammelsberg, *P.* 118, 158; Schiff, *A.* 107, 64). Two double compounds with $HgCl_2$, viz. $(NH_4)_2Cr_2O_7.HgCl_2.H_2O$, and $3(NH_4)_2Cr_2O_7.HgCl_2$, exist (Darly, *A.* 65, 204; Zepharovich, *Sitz. W.* 39, 17; Clarke a. Stern, *Am.* 3, 351).

Barium dichromate $BaCr_2O_7.2H_2O$; yellow needles, obtained by dissolving $BaCrO_4$ in conc. CrO_3Aq, evaporating, crystallising, and drying at 100°. Decomposed by H_2O to $BaCrO_4$ and CrO_3Aq (Bahr, *J. pr.* 60, 30; Zettnow, *P.* 144, 167; Preis a. Rayman, *B.* 13, 340).

Bismuth dichromate.—The salt $2(Bi_23CrO_4).Bi_2O_3$, obtained by ppg. $Bi3NO_3$ in HNO_3Aq by K_2CrO_4Aq, described as a basic bismuth chromate (p. 155), may perhaps be better regarded as basic bismuth dichromate $(BiO)_2Cr_2O_7$.

Calcium dichromate $CaCr_2O_7.3H_2O$; deliquescent, red, crystals; obtained by dissolving $CaCrO_4$ in CrO_3Aq and evaporating (Bahr, *J. pr.* 60, 60).

Copper dichromate $CuCr_2O_7.2H_2O$; brown-black, deliquescent, crystals; e. sol. in H_2O or alcohol; decomposed by hot H_2O with separation of $CuCrO_4.2CuO$; obtained by dissolving CuO_2H_2 in conc. CrO_3Aq, and evaporating (Droege, *A.* 101, 39).

Lead dichromate $PbCr_2O_7$. Brick red, crystalline, powder; by action of CrO_3Aq on $PbCrO$ (Preis a. Rayman, *B.* 13, 340).

Lithium dichromate $Li_2Cr_2O_7$; black-brown, deliquescent, crystals (Rammelsberg, *B. B.* 1865. 629).

Potassium dichromate $K_2Cr_2O_7$. S.G. $\underline{4^\circ}$ 2·692 (Joule a. Playfair, *C. J.* 1, 121; Schiff, *A.* 107, 64). M.P. about 400° (Tilden a. Shenstone, *T.* 1884. 84). S.H. ·186 (Kopp, *A. Suppl.* 3, 1 a. 289). C.E. (0°–100°) ·0122 (Joule a. Playfair, *C. J.* 1, 121). S. (0°) 4·9; (10°) 8·4; (40°) 29·2; (80°) 73; (100°) 102; (117°) 128·3; (129°) 153·8, (148°) 200·6; (180°) 262·7. S.G. of solution 6·08 parts in 100 water = 1·0405 at 19·5°, of 13·1 parts in 100 water = 1·0847; saturated solution boils at 104°; insol. alcohol (Kremers, *P.* 92, 497; 95, 110; 96, 39; Alluard, *C R.* 59, 600; Michel a. Kraft, *A. Ch.* [3] 41, 471; Tilden a. Shenstone, *T.* 175, 23).

Preparation.—Chrome-ironstone is heated, powdered, and mixed with K_2CO_3 and CaO; the mixture is heated to 150° until quite dry, then to bright redness, in presence of air, with frequent stirring. The fused mass is allowed to cool, and is then treated with a small quantity of boiling water; if the solution contains $CaCrO_4$ it is decomposed by adding K_2CO_3 and filtering from $CaCO_3$. Sufficient acid to change the K_2CrO_4 to $K_2Cr_2O_7$ is added, the liquid is evaporated and allowed to crystallise. The crystals are purified by recrystallisation from water.

Properties.—Large, red, triclinic, crystals; unchanged in air. Solution in water is acid to litmus, has a metallic taste, and is poisonous. Is rapidly changed by light in presence of organic matter; hence used in photography (Schwann, *D. P. J.* 199, 130). Decomposed at white heat to K_2CrO_4, O, and Cr_2O_3.

Reactions. Reduced by heating with C, S, or NH_4Cl; or with solid $H_2C_2O_4$ (Bothamley, *C. J.* 51, 159; Werner, *C. J.* 53, 602); $K_2Cr_2O_7Aq$ is reduced by SO_2Aq to Cr_23SO_4Aq, and by H_2S to Cr_2O_3 and S; NO is absorbed and after a time CrO_2 is ppd. (Vogel, *J. pr.* 77, 482). Heated with conc. H_2SO_4, K_2SO_4, Cr_23SO_4, H_2O, and O are produced; addition of 2 formula-weights H_2SO_4 to a boiling solution of one formula-weight $K_2Cr_2O_7$ produces pp. of orange-red $HKSO_4.K_2Cr_2O_7$, which is decomposed by H_2O (Schwarz, *D. P. J.* 186, 81). Solution of $K_2Cr_2O_7$ in conc. HClAq gives $CrO_2.Cl.OK$ (*q. v.*) on cooling. From a hot solution of the salt in 12 parts HNO_3Aq, carmine-red crystals of $Cr_2O_5.NO_2.OK$ (?$OK.CrO_2.O.CrO_2.NO_2$) separate on cooling; by re-crystallising this salt from HNO_3Aq, the salt $Cr_3O_8.NO_2.OK$ (?$OK.CrO_2.O.CrO_2.O.CrO_2.NO_2$) is obtained (Darmstädter, *B.* 4, 117). A double compound $K_2Cr_2O_7.HgCl_2$ is obtained by evaporating a mixture of its constituents (Darly, *A.* 65, 204; Hahn, *Ar. Ph.* [2] 99, 147).

Rubidium dichromate $Rb_2Cr_2O_7$; and *Sodium dichromate*, $M_2Cr_2O_7$; closely resemble $K_2Cr_2O_7$ (Piccard, *J. pr.* 86, 449; Grandeau, *A. Ch.* [3] 67, 155).

Silver dichromate $Ag_2Cr_2O_7$. By ppg. $K_2Cr_2O_7Aq$ by $AgNO_3$, or digesting moist Ag_2O with $K_2Cr_2O_7Aq$; somewhat soluble in H_2O, crystallising in red, triclinic, crystals; decomposed by boiling water; when strongly heated gives Cr_2O_3 and Ag (Freese, *P.* 140, 87; Warington, *P. M.* 11, 489; Teschemacher, *P. M.* 1, 345; Nason, *A.* 104, 126).

Thallium dichromate $Tl_2Cr_2O_7$. Red, crystalline, powder; insol. in H_2O; decomposed by conc. acid to $Tl_2Cr_3O_{10}$ (*q. v. infra*). Obtained by reaction of thallous salts with $K_2Cr_2O_7Aq$.

Tri-, Tetra-, and Hexa-Chromates: $M^I_2Cr_3O_{10}$, $M^I_2Cr_4O_{13}$, and $M^I_2Cr_6O_{19}$. Very few of these salts are known. $(NH_4)_2Cr_3O_{10}$, $K_2Cr_3O_{10}$, and $Tl_2Cr_3O_{10}$ are obtained by crystallising solutions of the dichromates in HNO_3Aq (Siewert, *Z. f. d. g. Naturwiss.* 19, 11; Bothe, *J. pr.* 46, 184; Hauer, *Sits. W.* 39, 439; Willm, *A. Ch.* [4] 5, 5). $K_2Cr_4O_{13}$ is obtained by long-continued digestion of $K_2Cr_3O_{10}$ in conc. HNO_3Aq (Siewert, *l.c.*). $(NH_4)_2Cr_6O_{19}.10H_2O$ was obtained by Rammelsberg (*P.* 94, 507) from a solution of $(NH_4)_2Cr_3O_{10}$.

Chromites. *Compounds of Cr_2O_3 with more positive metallic oxides.* A compound $2CaO.Cr_2O_3$ is obtained, according to Chancel (*C. R.* 43, 927), by the reaction between NH_3Aq and chrome-alum solution mixed with $CaCl_2$. By mixing solutions in KOHAq of Cr_2O_3 and PbO or ZnO, pps. are obtained of the composition $MO.Cr_2O_3$ (Pelouze, *A. Ch.* [3] 33, 5). Compounds of the form $MO.Cr_2O_3$, where M = Mn, or Zn, are also produced by fusing together the component oxides with B_2O_3 at a white heat; the compounds crystallise out on cooling; $ZnO.Cr_2O_3$ forms dark green octahedra, S.G. 5·309; $MnO.Cr_2O_3$, hard iron-grey octahedra, S.G. 4·87 (Ebelmen, *A. Ch.* [3] 33, 34). These compounds may be regarded as chromites, MCr_2O_4, *i.e.* salts of the hypothetical chromous acid $H_2Cr_2O_4$. Certain metallic oxides which are insoluble in KOHAq become soluble therein when mixed with $Cr_2O_3.xH_2O$; *e.g.* a mixture of $Cr_2O_3.xH_2O$ with 40 p.c. Fe_2O_3, 12·5 p.c. MnO, 20 p.c. CoO, or 25 p.c. NiO, is completely soluble in KOHAq; on the other hand Cr_2O_3 is completely ppd. by KOHAq in presence of 80 p.c. Fe_2O_3, 60 p.c. MnO, or 50 p.c. CoO or NiO (Church, *Ph. C.* 1853. 391).

Chromium, alloys of. An alloy of Cr with Al is described by Wohler (*A.* 106, 118) as very fusible, tin-white, crystals; becoming brittle after fusion; S.G. 4·9. Fremy (*C. R.* 44, 632) obtained an alloy with Fe by reducing chrome-ironstone with C, or by the action of Fe on Cr_2O_3 at a very high temperature; long needles, harder than steel. By the action of Na amalgam on $CrCl_3Aq$ an amalgam of Cr with Hg is produced (Vincent, *P. M.* [4] 24, 328; Schönbein, *P.* 112, 445).

Chromium, ammonio- salts of; or **Chrom-ammonium salts.** Freshly ppd. $Cr_2O_3.xH_2O$ dissolves in conc. NH_4ClAq containing NH_3Aq; on standing in air a reddish-violet powder is deposited; when this is dissolved in cold HClAq and excess of conc. HClAq is added, a rose-red crystalline powder is produced having the composition $Cr_2Cl_6.8NH_3.2H_2O$. By treating this salt with cold conc. H_2SO_4, a new compound $Cr_2Cl_2(SO_4)_2.8NH_3.2H_2O$ is produced; by the action of BaI_2Aq on this, the salt $Cr_2Cl_2I_4.8NH_3.2H_2O$ is formed; and from this, $Cr_2Cl_2Br_4.8NH_3.2H_2O$ may be obtained by the action of conc. HBrAq. Various other derivatives are known of the general form $Cr_2M_2.X_4.8NH_3.xH_2O$, in which M = Cl, Br, or I, and X = negative radicle, Cl, Br, I, NO_3, $\frac{CrO_4}{2}$, &c. The reactions of this series of compounds forbid us to regard them as ordinary double compounds of Cr_2M_6 with xNH_3; they are usually looked on as compounds of the hypothetical groups, *chlorochrom-*, *bromochrom-*, *iodochrom-tetrammonium*, with negative radicles Cl_4, $(NO_3)_4$, &c. On this supposition the formula $N_4H_8(NH_4)_4.(Cr_2M_2).X_4$ would represent the compounds in question; the names *chloro-* (bromo-, iodo-,) *chromtetrammonium chloride*, *bromide*, &c., are used. The less hypothetical formula $M_2Cr_2.8NH_3.X_4$ is also frequently employed to represent the chloro(&c.)chromtetrammonium compounds.

Six other series of chromammonio-compounds are known. They may all be represented by the general form $Cr_2.xNH_3.X_6$, where $x = 10$ or 12, and X = negative radicle; in some of these part of the X_6 is easily replaced by other radicles and part is not; in others the whole of the X_6 is easily replaced. If M represent the radicle which is replaced with difficulty, and X the radicle which is easily replaced, we get the developed general formula for the seven series of compounds $M_x.Cr_2.8(10 \text{ or } 12)NH_3.X_z$; where $x = 1$, or 2, and $z = 4$, 5, or 6. The second to seventh series may also be regarded as derived from the first (*i.e.* from the chloro(&c.)chromtetrammonium salts, by replacing H in $N_4H_8(NH_4)_4.(Cr_2M_2).X_4$ by the radicle NH_4. The following formulæ represent the seven series of compounds: -

(1) $M_2.Cr_2.8NH_3.X_4$ or $N_4H_8(NH_4)_4.(Cr_2M_2).X_4$
Chromtetrammonium salts.

(2) $M_2.Cr_2.10NH_3.X_4$ or $N_4H_6(NH_4)_6(Cr_2M_2).X_4$
Purpureochrom salts.

(3) $Cr_2.10NH_3.X_6$ or $N_4H_6(NH_4)_8.Cr_2.X_6$
Roseochrom salts.

(4) $M_2.Cr_2.10NH_3.X_4$ or $N_4H_6(NH_4)_6(Cr_2M_2)X_4$
Xanthochrom salts; ($M_2 = 2NO_2$).

(5) $Cr_2.12NH_3.X_6$ or $N_4H_4(NH_4)_8.Cr_2.X_6$
Luteochrom salts.

(6) & (7) $M.Cr_2.10NH_3.X_5$ or $N_4H_6(NH_4)_6(Cr_2M).X_5$
Rhodochrom and *Erythrochrom salts*; (M = OH).

The purpureo- and roseo- salts are isomeric, using the term in a rather wider sense than is given to it in organic chemistry as the molecular weights of none of these salts are known; $AgNO_3Aq$ pps. $\frac{4}{6}$ of the Cl from purpureochromium chloride in the cold, but all the Cl from roseochromium chloride; HNO_3Aq, HBrAq, &c., also removes $\frac{4}{6}$ of the Cl from the former salts; boiling HIAq, however, produces $I_2.Cr_2.10NH_3.I_4$ (*iodopurpureochromium iodide*); and by acting on this with dilute HClAq, $I_2.Cr_2.10NH_3.Cl_4$ (*iodopurpureochromium chloride*) is obtained. Purpureo- compounds, in which M_2 and X_4 are the same radicle (*e.g.* $Br_2.Cr_2.10NH_3.Br_4$, or $Cl_2.Cr_2.10NH_3.Cl_4$) easily change to roseo- compounds by standing in the air, or by heating. Xanthochromium chloride is obtained by the action of $NaNO_2Aq$ and dilute HNO_3Aq on $Cl_2.Cr_2.10NH_3.Cl_4$, or on $Cr_2.10NH_3.Br_6$. The three series, purpureo- luteo- and rhodo- salts, are obtained by more or less slowly oxidising Cr_2Cl_4 in NH_4ClAq in presence of NH_3Aq; the purpureo- and rhodo- salts are obtained by oxidising in presence of air, the luteo- salts in absence of air (*v. infra*). The roseo- and erythro- salts are obtained from the purpureo- and rhodo- respectively (*v. infra*). The rhodo- and erythro- salts are isomeric; the former change to the latter by standing in air (*v. infra*).

In the nomenclature of the chromtetrammonium and purpureochromium salts it is necessary to use prefixes, chloro-, bromo-, &c., to express the nature of the radicles M_2; thus chloropurpureochromium chloride, and bromopurpureochromium nitrate, are $Cl_2.Cr_2.10NH_3.Cl_4$, and $Br_2.Cr_2.10NH_3.(NO_3)_4$, respectively. In the other series prefixes are unnecessary.

It will suffice here to describe the chief compounds in each series. The principal references are Fremy, *A. Ch.* [4] 9, 431; Clève, *J. pr.* 76, 47, *Am. S.* [2] 49, 251; Jörgensen, *J. pr.* [2] 20, 105; 25, 83; 25, 321; 30, 1; Christensen, *J. pr.* [2] 23, 26; 24, 74; 25, 398.

I. Chromtetrammonium Series

$M_2.Cr_2.8NH_3.X_4.xH_2O$. *Chlorochromtetrammonium chloride* $Cl_2.Cr_2.8NH_3.Cl_4.2H_2O$. Deep-red, very lustrous, almost opaque, trimetric crystals. Obtained by digesting freshly ppd. chromium hydroxide in a closed flask with conc. NH_4Cl in NH_3Aq, until the hydroxide dissolves: the deep-red liquid is allowed to stand in the air, the dark-violet powder which separates is dissolved in cold HClAq, excess of conc. HClAq is added, the rose-red crystalline powder which separates out is washed with conc. HClAq, then with strong alcohol, and is crystallised from warm H_2O containing a little HCl. This compound begins to decompose at 120°; when strongly heated NH_3, NH_4Cl, and H_2O, are given off, and Cr_2O_3 remains; heated in air-free H, or in CO_2, Cr_2OCl_4 remains. The salt is soluble in water, but on boiling $Cr_2O_3.xH_2O$ and NH_3 are produced. Treated with H_2O and moist Ag_2O, a liquid is obtained probably containing $Cl_2.Cr_2.8NH_3.(OH)_4$; it soon decomposes with evolution of NH_3.

The *sulphate* $Cl_2.Cr_2.8NH_3.(SO_4)_2.2H_2O$ is obtained by treating the chloride with cold conc. H_2SO_4, and then with H_2O; from this the *iodide* ($X_4 = I_4$) is produced by the action of BaI_2Aq, and by the action of fuming HBrAq on this, the *bromide* ($X_4 = Br_4$) is produced.

If freshly ppd. $Cr_2O_3.xH_2O$ is treated with NH_4Br in NH_3Aq, *bromochromtetrammonium bromide*, $Br_2.Cr_2.8NH_3.Br_4.2H_2O$ is produced; an aqueous solution of this salt dropped into conc. HClAq gives the *bromo-chloride* ($M_2 = Br_2$, $X_4 = Cl_4$).

II. Purpureochromium series

$M_2.Cr_2.10NH_3.X_4$. *Chloropurpureochromium chloride*. $Cl_2.Cr_2.10NH_3.Cl_4$. Prepared by reducing $K_2Cr_2O_7$ by alcohol and very conc. HClAq, so that 12g. $K_2Cr_2O_7$ give 50 c.c. $CrCl_3$ solution, pouring the liquid (from KCl) through a separating funnel into a cylinder fitted with a reversed U-tube and an exit tube, and containing sticks of Zn, and adding a little HClAq; when the liquid is the colour of $CuSO_4Aq$ (which indicates reduction to $CrCl_2$), forcing it through the U-tube into a solution of 600 g. NH_4Cl in 1,000 c.c. NH_3Aq, S.G. ·9; and repeating this operation until 50 g. $K_2Cr_2O_7$ have been reduced, and the $CrCl_3$ solution further reduced to $CrCl_2$ and driven into the ammoniacal NH_4ClAq. The blue liquid is then oxidised, by long-continued passage of air, until it becomes deep carmine-red; 2½ litres of conc. HClAq are added, the liquid is boiled for a few minutes, when the chloride separates out as a carmine-red crystalline powder. This liquid is allowed to cool, and poured off, the residue is washed free from NH_4Cl by conc. HClAq + an equal volume of H_2O, collected on a filter and again washed with the same HClAq, dissolved in H_2O slightly acidified with H_2SO_4, and re-ppd. by conc. HClAq; the pp. is boiled with a little conc. HClAq, washed with the same strength of HClAq as before, then with 90 p.c. alcohol, and dried at about 18°–20°.

Chloropurpureo-chromium chloride crystallises in small carmine-red octahedra: S.G. $\frac{15.5^\circ}{}$

1·687; S. (16°) ·65; insol. conc. **HClAq**; on boiling an aqueous solution roseochromium chloride is obtained; decomposed by heat, giving Cr_2O_3.

Bromo-bromide ($M_2 = Br_2$, $X_4 = Br_4$) is prepared similarly to the chloro-chloride, using NH_4Br in place of NH_4Cl, &c. By treatment with excess of HClAq it yields *bromo-chloride* ($M_2 = Br_2$, $X_4 = Cl_4$). By treating chloro-chloride with boiling conc. HIAq *iodo-iodide* ($M_2 = I_2$, $X_4 = I_4$) is formed. By the action of dilute HNO_3Aq, H_2SO_4Aq, &c., on chloro-chloride, *chloro-nitrate*, *chloro-sulphate*, &c., are obtained ($M_2 = Cl_2$, $X_4 = 4NO_3$, $2SO_4$, &c.); the action of K_2CrO_4Aq produces *chloro-chromate* ($M_2 = Cl_2$, $X_4 = 2CrO_4$). Besides these the following compounds have been prepared:—

M_2	X_4	M_2	X_4	M_2	X_4
Cl_2	$2SiF_6$	Br_2	$2PtBr_6$	I_2	Cl_4
		Br_2	$4NO_3$	I_2	$4NO_3$
		Br_2	$2CrO_4$	I_2	$2PtCl_6$

III. ROSEOCHROMIUM SERIES $Cr_2.10NH_3.X_6$. *Roseochromium chloride*, $Cr_2.10NH_3.Cl_6$. Obtained by rubbing 5 g. dry chloropurpureochloride with the moist Ag_2O from 20 g. $AgNO_3$ for a few minutes in a mortar, filtering, neutralising the alkaline liquid with HClAq, filtering from AgCl, evaporating in a rapid air-stream, pressing pp. between paper, washing once with a little H_2O, and drying in air out of direct sunlight. Orange-yellow crystals; v. sol. H_2O; insol. alcohol; very unstable, giving off NH_3; changed, as are all roseo- salts, by heating with conc. HClAq, to purpureo- salt. $AgNO_3Aq$ pps. all the Cl in the cold.

The other roseo- salts are formed by neutralising the solution obtained by action of moist Ag_2O on purpureo-chloride by various acids; the solution in question probably contains roseohydroxide [$X_6 = (OH)_6$]. The chief roseo- salts are $X_6 = Br_6$, I_6, $3SO_4$, $6NO_3$, $Br_2(PtBr_6)_2$, $(SO_4)_2PtCl_6$, $Br_2(CrO_4)_2$.

IV. XANTHOCHROMIUM SERIES $(NO_2)_2.Cr_2.10NH_3.X_4$. *Xanthochromium chloride*, $(NO_2)_2.Cr_2.10NH_3.Cl_4$. To 20 g. chloropurpureochloride 300 c.c. warm water and about 20 drops dilute HNO_3Aq are added, the liquid is slowly heated to boiling, then cooled, and filtered; the insoluble purpureo-chloride is again treated in the same way; 40–50 g. *pure* $NaNO_2$ and 25 c.c. HClAq (12 p.c.) are added to the total liquid; the yellow crystalline salt which separates out is washed with water, then with alcohol, dissolved in water, and ppd. by fairly conc. NH_4ClAq. Xantho-chloride is a yellow crystalline powder; fairly sol. H_2O; insol. alcohol; easily decomposed by acids with production of HNO_2; treated with HClAq, chloropurpureo-chloride is formed; fairly stable towards alkalis; forms double salts with $2PtCl_4$ and $4HgCl_2$.

The other most important xantho- salts are: $X_4 = Br_4$, I_4, $2SO_4$, $2S_2O_3$, $4NO_3$, $2CO_3$, $2CrO_4$; the hydroxide, $X_4 = (OH)_4$, is known in aqueous solution, it is fairly stable, and has a strongly alkaline reaction.

V. LUTEOCHROMIUM SERIES $Cr_2.12NH_3.X_6$. *Luteochromium nitrate*, $Cr_2.12NH_3.(NO_3)_6$. 80 g. $K_2Cr_2O_7$ are reduced to $CrCl_2$ by the method described under chloropurpureochromium chloride; the solution is forced by H pressure into a flask containing 700 g. NH_4Cl in 750 c.c. NH_3Aq (S.G. ·91); the flask, which must be entirely filled with the liquid, is closed by a cork carrying an exit tube opening under water, and is surrounded by cold water; after about 24 hrs. evolution of H ceases; the liquid is poured off from ppd. luteo-chloride and NH_4Cl, and is ppd. by alcohol; the crude luteo-chloride is washed with alcohol, dried, dissolved in warm water, and the solution is filtered into HNO_3Aq (S.G. 1·39); the crystals of luteo-nitrate are washed with dilute HNO_3Aq (1 vol. conc. HNO_3Aq to 2 vols. H_2O), and then with alcohol. The pp. of mixed NH_4Cl and luteo-chloride formed in the process may be dissolved by repeated treatment with H_2O, and luteo-nitrate obtained by ppn. with HNO_3Aq. Luteo-nitrate crystallises in orange-yellow, lustrous plates; S. (abt. 15°) 2·5; insol. alcohol; nearly insol. dilute HNO_3Aq.

The luteo-chromium salts form many double compounds with acid radicles, and also with some negative metallic radicles; the more important salts are:—$X_6 = 2NO_3.2SO_4$, $2NO_3.2PtCl_6$, Cl_6, Br_6, I_6, $Cl_4.H_2PtCl_6$, $Cl_2.2PtCl_6$, $3PtCl_6$, $3PtBr_6$, $I_2.2SO_4$, $3SO_4$, $2SO_4.PtCl_6$, $3C_2O_4$, $2NaP_2O_7$, $Fe_2(CN)_{12}$, $Co_2(CN)_{12}$, $Cr_2(CN)_{12}$ (Jörgensen, *J. pr.* [2] 30, 1).

VI. RHODOCHROMIUM SERIES $OH.Cr_2.10NH_3.X_5$. *Rhodochromium bromide*, $OH.Cr_2.10NH_3.Br_5.H_2O$. $Cr_2O_3.xH_2O$, equal to 10 g. Cr_2O_3, is dissolved in 100 c.c. conc. HBrAq; the green solution is poured on to Zn in a cylinder arranged with a reversed U-tube, &c., as described under purpureochloride; 30 c.c. HBrAq (1 vol. conc. solution + 1 vol. H_2O) are added; when the liquid is blue (after about 10 min.) 30 c.c. of the same HBrAq are added, and the H pressure is caused to force the liquid into 150 g. NH_4Br in 750 c.c. conc. NH_3Aq; the blue solution is oxidised by a stream of air, after all particles of Zn have been removed; the liquid is quickly decanted from the blue pp. (basic rhodo-bromide), which is treated with excess of HBrAq (1 vol. conc. solution + 3 vols. H_2O), whereby red rhodo-bromide is formed; the salt is washed with dilute HBrAq and then with water, it is then dissolved in cold water and the liquid is poured into moderately dilute HBrAq; the crystals which separate are washed with dilute HBrAq and then with alcohol, and are dried in the air. Dried for some days over H_2SO_4 they lose their H_2O. Rhodo-bromide is a pale carmine-red crystalline powder; slowly loses its H_2O over conc. H_2SO_4; sl. sol. cold H_2O; on warming, the solution goes blue-violet; on boiling, NH_3 comes off, and $Cr_2O_3.xH_2O$ pps.; insol. dilute HBrAq and NH_4BrAq; boiled with very dilute HBrAq it is changed to roseochromium bromide; boiled with conc. HBrAq it gives brompurpureo-bromide; with $AgNO_3$ all the Br is ppd.; dilute NaOHAq or NH_3Aq removes $\frac{1}{5}$ Br, and a basic rhodo- salt remains; dilute acids form the respective rhodo-salts.

The chief rhodo- salts known are:—$X_5 = Cl_5$, I_5, $5NO_3$, $2\frac{1}{2}CO_3$, $2\frac{1}{2}SO_4$, $2\frac{1}{2}S_2O_6$, $Cl_3.2AuCl_4$, $Cl_3.PtCl_6$, $Cl.2PtCl_6$; and the basic salts:—$X_5 = OH.Br_4$, $OH.Cl_2I_2$, $OH.2S_2O_6$ (Jörgensen, *J. pr.* [2] 25, 321).

VII. ERYTHROCHROMIUM SERIES $OH.Cr_2.10NH_3.X_5$. *Erythrochromium nitrate*, $OH.Cr_2.10NH_3.5NO_3.H_2O$. Rhodo-chloride is prepared by filtering a solution of rhodo-bromide into HClAq (1 vol. conc. solution + 1 vol. H_2O); it is washed with alcohol, 5 g. rhodo-chloride are dissolved in 50 c.c. H_2O + 35 c.c. dilute NH_3Aq; when the blue solution has become red by standing in air 4–5 vols. of dilute HNO_3Aq are added; the pp. is repeatedly treated with dilute HNO_3Aq, dissolved in H_2O, reppd. by HNO_3Aq, washed with alcohol, and dried in the dark. Erythrochromium nitrate is a crimson powder composed of microscopic octahedra; it decomposes slowly even in the dark; when strongly heated N oxides are evolved and Cr_2O_3 remains; fairly sol. cold water; insol. alcohol; aqueous solution decomposes when boiled with separation of $Cr_2O_3.xH_2O$; aqueous solution boiled with a few drops of HNO_3Aq gives roseochromium nitrate; solid erythronitrate boiled with dilute HClAq gives chlorpurpureo-chloride.

Other salts are obtained by the action of acids on the bromide or chloride; the principal are:—$X_5 = Br_5$, ClI_4, $2\frac{1}{2}SO_4$; and the basic salts $X_5 = OH.Br_4$, $OH.4NO_3$, $OH.2S_2O_6$ (Jörgensen, *J. pr.* [2] 25, 398).

Chromium, arsenates of.—Existence uncertain (*v.* ARSENATES, under ARSENIC, ACIDS OF; vol. i. p. 308).

Chromium, bromides of.—Two are known; as neither has been gasified the formulæ $CrBr_2$ and $CrBr_3$ may or may not represent the composition of the gaseous molecules; judging from the analogy of $CrCl_3$ it is probable that the formulæ $CrBr_2$ and $CrBr_3$ are molecular. These compounds resemble the chlorides (*q. v.*) in their properties.

I. CHROMOUS BROMIDE $CrBr_2$ or Cr_2Br_4. Obtained as white crystals by heating $CrBr_3$ in H, by leading HBr over heated Cr, or by the action of N saturated with Br vapour on Cr at a red heat (Moissan, *A. Ch.* [5] 25, 401). Unchanged in dry air, but oxidises in presence of traces of moisture; dissolves in H_2O forming blue liquid, which dissolves large quantities of violet $CrCl_3$.

II. CHROMIC BROMIDE $CrBr_3$ or Cr_2Br_6. Small cylinders formed of Cr_2O_3, C, and starch paste, are dried and heated to redness in a covered crucible; they are then heated in a tube of hard glass in dry Br vapour; crystals of $CrBr_3$ sublime, and some remain mixed with, but easily separable from, Cr_2O_3. Dark, metal-like, lustrous, hexagonal crystals; olive-green by transmitted light, slightly dichroïc in red light (Wöhler, *A.* 111, 382). Heated in air Cr_2O_3 is formed; KOHAq or NaOHAq decomposes $CrBr_3$ into Cr_2O_3 and KBrAq or NaBrAq. Insol. in H_2O, but dissolves in presence of a little $CrBr_2$. A green solution containing $CrBr_3$ is obtained by the action of HBrAq on $Cr_2O_6H_6$.

Chromium, chlorides of.—Two exist, $CrCl_2$ and $CrCl_3$. Chromic chloride has been gasified (at 1200°-1500°) and the observed V.D. corresponds with the formula $CrCl_3$; it is probable, but not certain, that the molecular formula of chromous chloride is $CrCl_2$.

$CrCl_3$, like several other compounds of Cr, exists in two forms; one sol., the other insol. in H_2O. $CrCl_2Aq$ is an energetic reducer. Solutions of CrO_2 and CrO_3 in cold conc. HClAq may contain $CrCl_4$ and $CrCl_6$ respectively; these solutions are brown, they evolve Cl when heated, and $CrCl_3$ remains.

I. CHROMOUS CHLORIDE $CrCl_2$ or Cr_2Cl_4. Mol. w. unknown.

Formation.—1. By the action of dry HCl on Cr at a red heat (Ufer, *A.* 112, 302; Moissan, *A. Ch.* [5] 25, 401).—2. By heating $CrCl_3$ with NH_4Cl to a very high temperature (Moissan, *l.c.*).

Preparation.—Violet, sublimed $CrCl_3$ is heated in a stream of perfectly dry H, free from every trace of O, to a very low red heat; the reduction takes place very slowly, but the temperature must not be raised, else some Cr will be formed (Moberg, *J. pr.* 29, 175; 43, 125; 44, 322; Péligot, *A. Ch.* [3] 12, 528). The H used should be passed through a solution of $SnCl_2$ in KOHAq, then through conc. H_2SO_4, then over red hot Cu, and lastly through boiled H_2SO_4 and over $CaCl_2$.

Properties.—White lustrous crystals; sol. in H_2O, with production of heat, forming a blue liquid, which rapidly absorbs O turning green. Péligot determined the quantity of O absorbed; it corresponded with formation of Cr_2Cl_4O. Loewel (*A. Ch.* [3] 40, 42), by the prolonged action of granulated Zn on a solution of $CrCl_3.6H_2O$ in 3–5 parts H_2O in a flask nearly filled with the Zn, obtained a colourless solution of $CrCl_2$ (containing Zn), which acted as a strong reducer; *e.g.* K_2CrO_4Aq was reduced to CrO_2, $HgCl_2Aq$ to HgCl, $CuSO_4Aq$ to Cu_2Cl_2 and Cu_2O, and solutions of Au and Sn salts to Au and Sn.

Reactions.—$CrCl_2Aq$ protected from air gives the following reactions:—1. With *potash* or *soda*, brownish-yellow CrO_2H_2, which quickly becomes CrO_3H_3 with evolution of H.—2. *Potassium sulphide* pps. black Cr_2S_3.—3. *Sodium acetate* forms a red liquid from which red lustrous crystals of $Cr(C_2H_3O_2)_2.H_2O$ separate after a time.

Combinations.—1. With *water*, to form $2CrCl_2.3H_2O$ (Moissan, *A. Ch.* [5] 25, 401).—2. With dry *hydrochloric acid*, to form an easily decomposed compound $6CrCl_2.4HCl.26H_2O$ (Recoura, *C. R.* 100, 1227).

II. CHROMIC CHLORIDE $CrCl_3$. Mol. w. 158·55. V.D. 77·45 (Scott, *Pr. E.* 14, 410).

Formation.—By heating Cr_2S_3 in dry Cl (Berzelius, *P.* 50, 79; Brunner, *D. P. J.* 159, 356).

Preparation.—An intimate mixture of Cr_2O_3 and lampblack is made into little pellets with starch paste; the pellets are dried and heated in a covered crucible, they are then placed in a Hessian crucible, through the bottom of which is fitted a porcelain tube about 6 inches long; the upper end of this tube, which passes a very little way into the crucible, is loosely covered with a very small crucible to prevent the pellets falling into the tube; into the mouth of the Hessian crucible is fitted a smaller crucible, inverted, and pierced by a hole. The crucibles are arranged in a furnace, so that the lower one may be heated very highly and the upper kept comparatively cool. The porcelain tube is connected with a supply of dry Cl. The pellets are now heated in a rapid stream of Cl; $CrCl_3$ sublimes into the upper crucible; the whole is allowed to cool in Cl, else Cr_2O_3 may be formed. The sublimate is washed with cold H_2O to remove Al_2Cl_6 formed from the crucible (Wöhler, *A.* 111, 230; Ufer, *A.* 112, 281).

Properties. — Lustrous, peach-blossom coloured plates. S.G. 3·03 (Schafarik, *J. pr.* 90, 12). Decomposed at high temperature without fusion with evolution of Cl (Carnelley a. Williams, *C. J.* 37, 126). Insol. in water, unacted on by acids, even by *aqua regia*. $CrCl_3$ may be obtained in soft violet-coloured plates, v. sol. in H_2O, by dissolving green CrO_3H_3 in HClAq, evaporating slowly until crystals of $CrCl_3.6H_2O$ separate, and heating these in HCl or Cl not above 250° (Moberg, *J. pr.* 44, 325; Péligot, *J. pr.* 37, 475). $CrCl_3$ thus prepared dissolves very easily in H_2O, forming a green solution; heated above 250° the salt sublimes to crystals of the peach-blossom coloured, insoluble variety. The latter crystals when powdered and boiled with water for some time go into solution with production of a green liquid (Jacquelin, *C. R.* 24, 679).

A violet solution of $CrCl_3$ is produced by decomposing violet Cr_23SO_4Aq by an equivalent quantity of $BaCl_2Aq$. When this solution is boiled it becomes green.

The green solutions evaporated at 100° give crystals of $CrCl_3.xH_2O$ (*v. Combinations*, No. 1); the same green hydrates of $CrCl_3$ are obtained by dissolving green CrO_3H_3 in HClAq, or the insoluble $CrCl_3$ in H_2O containing a trace of $CrCl_2$, or $PbCrO_4$ in conc. HClAq and reducing by alcohol, and evaporating at about 100°; evaporated at higher temperatures oxy-chlorides (*q. v.*) are obtained. These green solutions probably therefore contain $CrCl_3$. But only two-thirds of the total Cl is ppd. from them in the cold by $AgNO_3Aq$; on boiling for some time the rest of the Cl also forms AgCl. On the other hand, $AgNO_3Aq$ pps. all the Cl from the violet-coloured solution of $CrCl_3$ obtained by the action of $BaCl_2Aq$ on violet Cr_23SO_4Aq. Moreover, green-coloured double chlorides, $MCl.CrCl_3$, where M = alkali metal, are not obtained, whereas several violet double chlorides are known (*v. Combinations*, No. 2). Péligot (*J. pr.* 37, 475) supposed that a green solution of $CrCl_3$ contains CrOCl and HCl; Berzelius (*P.* 50, 79) supposed that on adding $AgNO_3$ a double compound of AgCl and $CrCl_3$ is formed and that this is decomposed only on boiling.

Reactions.—1. Finely powdered $CrCl_3$ boiled for some time with *water* slowly dissolves, forming a green solution (Jacquelin, *C. R.* 24, 679). If the water contains $\frac{1}{1000}$ to $\frac{1}{4000}$ of its weight of $CrCl_2$, or a little $SnCl_2$ or Cu_2Cl_2, the $CrCl_3$ quickly dissolves with production of much heat, forming a green liquid with the same reactions as that obtained by dissolving CrO_3H_3 in HClAq (Péligot, *J. pr.* 36, 150; Loewel, *J. pr.* 37, 150; Pelouze, *P.* 24, 233; Moberg, *A.* 109, 82; Barreswill, *A. Ch.* 12, 528) (*v. Combinations*, No. 1; also CHROMIUM, OXYCHLORIDES OF).—2. Boiled with *potash* or *soda* $CrCl_3$ is slowly decomposed with formation of Cr_2O_3.—3. Fused with *nitre and an alkali or alkaline carbonate* chromate and chloride of the alkali metal are formed.—4. Molten *potassium dichromate* forms $CrO_2.Cl.OK$ (Geuther, *A.* 118, 61).—5. Heated with *chromic anhydride* Cr_2O_3 and CrO_2Cl_2 are produced.—6. Heated in *air* Cr_2O_3 results.—7. Heated in dry *hydrogen* $CrCl_2$, and then Cr, is formed.—8. *Zinc* or *potassium* reduces $CrCl_3$ to Cr when heated with it.—9. Heated in *ammonia* CrN is formed.—10. Heated in *phosphoretted hydrogen* CrP results.—11. Heated in *sulphuretted hydrogen* or with *sulphur* the product is Cr_2S_3.

Combinations.—1. With *water*, to form various green, crystalline, easily soluble hydrates:—$2CrCl_3.9H_2O$, by evaporating CrO_3H_3 in HClAq in dry air at 100° (Moberg, *J. pr.* 29, 175); $CrCl_3.6H_2O$, by evaporating (1) violet $CrCl_3$ in H_2O containing a trace of $CrCl_2$ in dry air, or (2) solution obtained by action of conc. HClAq and alcohol on $PbCrO_4$ (Péligot, *J. pr.* 37, 475; Moberg, *J. pr.* 44, 326). Godefroy (*Bl.* [2] 43, 229) describes also $CrCl_3.10H_2O$, and $CrCl_3.4H_2O$, as green crystals. One or other of these hydrates is probably formed when violet $CrCl_3$ dissolves in H_2O containing a trace of $CrCl_2$; Loewel (*J. pr.* 37, 150) supposes that the $CrCl_3$ is reduced to $CrCl_2$ by the action of the $CrCl_2$ present, and that the $CrCl_3$ thus formed combines with H_2O and dissolves as $CrCl_3.xH_2O$, and that more $CrCl_3$ is reduced by the freshly formed $CrCl_2$, and so on (*v.* also Recoura, *C. R.* 102, 921). According to Recoura (*C. R.* 102, 513 a. 548) the hydrate $2CrCl_3.13H_2O$ exists in two varieties: (1) green crystals, produced by passing HCl into a saturated solution of green $CrCl_3$ (or by passing air into cooled $CrCl_2Aq$ containing much HCl, and then passing in HCl; *C. R.* 102, 921); (2) greyish blue crystals, produced by heating a solution of 1 pt. of the green crystals in 1 pt. water, and then saturating with HCl. The green crystals dissolve in water (S. = 130) without production of heat; the greyish blue crystals dissolve very readily in water with production of much heat $[2CrCl^3.13H^2O, Aq] = 24,000$. — 2. With *alkali chlorides* to form double salts $MCl.CrCl_3$, the properties of which are little known; prepared by treating $M_2Cr_2O_7$ (M = K, Na, or NH_4) with HClAq and alcohol, and evaporating at 100° until the residue is violet. On adding H_2O solution occurs, the liquid is yellow-red, but soon becomes green. Godefroy (*Bl.* [2] 42, 194) says that various double metallic chlorides containing $CrCl_3$ may be obtained by passing Cl into a mixture of metallic chromate and alcohol, and washing the products with HClAq; these double salts are decomposed by H_2O, but are unchanged in HClAq containing 32½ p.c. HCl.—3. With *phosphoric chloride* to form $2CrCl_3.2PCl_5$; obtained by heating the constituent chlorides in a sealed tube, and then to 140°–150° in an open vessel (Cronander, *B.* 6, 1466).—4. With *ammonia* to form several compounds (*v.* CHROMIUM, AMMONIO-SALTS OF).

Chromium, cyanides of, and their derivatives *v.* CYANIDES.

Chromium, fluorides of. Only one is known with fair certainty. CrF_3 is described by Deville (*C. R.* 43, 970) as forming lustrous, monometric, octahedra; obtained by dissolving dry CrO_3H_3, which has not been strongly heated, in HFAq, evaporating in a Pt dish, and heating the green mass to a very high temperature. The double salts $CrF_3.2MF.H_2O$, where M = Na, K, or NH_4, are described by Wagner (*B.* 19, 896).

Unverdorben (*P.* 7, 311) obtained a red gas by heating fluorspar and $PbCrO_4$ with conc. H_2SO_4. Dumas (*A. Ch.* [2] 31, 435) prepared the compound as a deep red liquid, by warming 4 pts. dry $PbCrO_4$, 3 pts. dry pure CaF_2, and 5–7 pts. very conc. H_2SO_4, in a retort of Pt or Pb, and leading the gas through a well-cooled tube of Pt and Pb into a Pt receiver. The liquid is volatile; the vapour acts on the mucous membranes and produces violent coughing; it is at once decomposed in ordinary air, or by H_2O, to HF and CrO_3; it acts rapidly on glass, forming SiF_4

The formula CrF_6 was given from estimations of the quantities of CrO_3 and HF produced by leading the gas into water. Rose (*P.* 27, 565) found more F than agreed with CrF_6. Oliveri (*G.* 16, 218) recently examined this supposed fluoride; according to him it is an oxyfluoride CrO_2F_2 analogous to CrO_2Cl_2.

Chromium, hydrated oxides of, *v.* Chromium, hydroxides of.

Chromium, hydroxides of. Several compounds of Cr with H and O are known. They react rather as hydrated oxides than as hydroxides (*v.* art. Hydroxides). Chromous hydroxide, or hydrated chromous oxide, $CrO_2H_2(CrO.H_2O)$ is very easily oxidised; it behaves towards acids as a salt-forming compound. At least three hydrates of Cr_2O_3 are known:—

$Cr_2O_3.7H_2O(Cr_2O_6H_6.4H_2O)$,
$Cr_2O_3.4H_2O(Cr_2O_6H_6.H_2O)$,

and $Cr_2O_3.H_2O(Cr_2O_2.O_2H_2)$; these compounds are all salt-forming in their reactions with acids, but at the same time they exhibit feebly acidic functions. The hydrate $CrO_3.H_2O(CrO_2.O_2H_2)$ is a strongly marked acid.

The hydrates of Cr are more or less easily separated into oxide and H_2O by the action of heat; the oxide Cr_2O_3 does not directly combine with water; CrO_3 readily combines with H_2O, but the solution is separated into CrO_3 and H_2O by boiling; the action of CrO towards H_2O is not known as the oxide has not been prepared.

I. Chromous hydroxide. CrO_2H_2 or $CrO.H_2O$. It is doubtful whether this compound has been obtained quite free from $Cr_2O_3.xH_2O$. A solution of $CrCl_2$ in air-free water, and protected from air, gives a yellowish-brown pp. with KOH dissolved in air-free H_2O (Moberg, *J. pr.* 43, 114 a. 125). The hydroxide quickly absorbs O and becomes dark brown; it rapidly decomposes H_2O, and combines with part of the O evolved. CrO_2H_2 is slowly dissolved by acids with separation of Cr and formation of chromous salts CrX_2, *e.g.* $CrSO_4.7H_2O$, $Cr(C_2H_3O_2)_2.H_2O$, &c.; these salts are unstable, and readily oxidise to chromic salts CrX_3 (Moberg, *J. pr.* 41, 330; Péligot, *A.* 52, 247) (*v.* Chromium, salts of, p. 167).

II. Chromic hydroxides. *Preparation.*—A clear blue pp. of $Cr_2O_3.xH_2O$ is obtained by the action of NH_3Aq on $CrCl_3Aq$ at the ordinary temperature. The $CrCl_3Aq$ must be perfectly free from any fixed alkali; it is prepared by dissolving Cr in HClAq, or $CrCl_3$ in H_2O containing a trace of $CrCl_2$, or by reducing CrO_3 by HClAq. When the pp. is thoroughly washed and dried over sulphuric acid the compound $Cr_2O_3.7H_2O(Cr_2O_6H_6.4H_2O)$ is obtained; when dried *in vacuo* $Cr_2O_3.4H_2O(Cr_2O_6H_6.H_2O)$ remains; and when dried at 200°–220° in H, the compound $Cr_2O_3.H_2O(Cr_2O_2.(OH)_2)$ is produced (Siewert, *Z. f. d. ges. Naturwiss.* 18, 244).

For accounts of the earlier experiments on composition of the various $Cr_2O_3.xH_2O$ *v.* Lefort, *J. pr.* 51, 261; Hertwig, *A.* 45, 298; Schaffner, *A.* 51, 168; Fremy, *C. R.* 47, 883; Ordway, *Am. S.* [2] 26, 197; Mitscherlich, *Lehrb. d. Chem.* [4th ed.] 2, 751; Vincent, *P. M.* [4] 13, 191).

The pp. obtained by the action of KOHAq or NaOHAq on $CrCl_3Aq$, or on solutions of other chromic salts, contains alkali which cannot be removed by hot water.

Graham (*T.* 1861. 183), by long-continued dialysis of solution of freshly ppd. $Cr_2O_3.xH_2O$ in $CrCl_3Aq$, obtained a liquid containing 1·5 pts. HCl to 98·5 $Cr_2O_3(=HCl:31{\cdot}2Cr_2O_3:xH_2O)$; this solution, which may be taken as nearly pure $Cr_2O_3.xH_2O$ dissolved in water, was unchanged on dilution or boiling, but was coagulated by addition of traces of salts, with separation of $Cr_2O_3.xH_2O$.

A green hydrate—approximately pure $Cr_2O_3.2H_2O$—known as Guignet's green, is obtained by heating 10 pts. $K_2Cr_2O_7$ and 18 pts. crystallised boric acid to low redness, and treating with H_2O. It is scarcely soluble in boiling HClAq (*v.* Scheurer-Kestner, *Bl.* 1865. 23; Salvétat, *C. R.* 48, 295).

Properties and Reactions.—Any of the hydrates $Cr_2O_3.xH_2O$ heated to 200° in air takes up O, forming a black powder, which reacts with HClAq evolving Cl, and from which H_2O dissolves out CrO_3 (Siewert, *l.c.*; Krüger, *A.* 52, 219). The three hydrates where $x=7$, 4, or 1, are hygroscopic; $Cr_2O_3.H_2O$ is insol. in boiling dilute HClAq, the two others dissolve in acids forming chromic salts, CrX_3 (*v.* Chromium, salts of). The hydrates are sol. in KOHAq, but on standing or boiling they are reppd., and the pps. contain alkali; they are sl. sol. in NH_3Aq, but are reppd. on boiling.

The hydrates $Cr_2O_3.xH_2O$ react towards acids as salt-forming hydroxides; but they also exhibit slightly acidic functions. Thus, the pps. obtained by adding KOHAq to solutions of chromic salts cannot be washed free from alkali even by hot water. Also, NH_3Aq added to solution of a chromic salt mixed with a salt of Ca or Zn, &c., forms a pp. containing Cr_2O_3 and CaO or ZnO, &c. (Pelouze, *A. Ch.* [3] 33, 5). Solution of PbO or ZnO in KOHAq, mixed with solution of $Cr_2O_3.xH_2O$ in KOHAq, yields a pp. of $MO.Cr_2O_3$ (Chancel, *C. R.* 43, 927). By long digestion of $Cr_2O_3.xH_2O$ in conc. NH_3Aq a dark-blue compound of Cr_2O_3 with NH_3 is produced, insol. in water, but sol. in HClAq (*v.* Chromites; and Chromium, ammonio-salts of).

Chromium, iodides of. Very little is known regarding these compounds. None seems to have been definitely isolated (*v.* Walz, *C. N.* 26, 245). Moissan (*A. Ch.* [5] 25, 401) describes CrI_2, or Cr_2I_4, as a white salt, sol. in water with formation of blue liquid; obtained by the action of HI, or I vapour, on heated Cr.

Chromium, nitride of, CrN. Mol. w. unknown.

Preparation.—1. Finely powdered Cr is heated to whiteness in N; the metal is again powdered and heated in N, and this process is repeated several times. Unchanged Cr is dissolved out by conc. HClAq (Briegleb a. Geuther, *A.* 123, 228).—2. $CrCl_3$ dried at about 120° is strongly heated in dry NH_3, the process being repeated several times; the residual $CrCl_3$ is removed by long digestion in conc. HClAq in contact with Sn ($CrCl_2$ is formed and dissolved); the product is washed, and dried at 100°–120° (Ufer, *A.* 112, 281; *v.* also Liebig, *P.* 21, 359; Schrotter, *A.* 37, 148; Gmelin, *Gm.* 4, 139).

Properties and Reactions.—Heavy, black, amorphous powder. Heated to about 1500° in absence of air, it is decomposed to Cr and N (Ufer, *A.* 112, 281). It is unacted on by KOHAq.

by dilute acids, by conc. HClAq or HNO_3, by H, by steam, or by molten Na_2CO_3; *aqua regia* dissolves it slowly; cold conc. H_2SO_4 dissolves it with formation of $Cr_2(NH_4)_2(SO_4)_4.24H_2O$, and without evolution of N. Heated in HCl gas, $CrCl_3$ and NH_4Cl are formed. Slowly sol. in solutions of alkaline hypochlorites, with formation of alkaline chromates and N; decomposed by molten KNO_3, or $KClO_3$, with formation of K_2CrO_4 and N (Ufer, *l.c.*); decomposes NH_3 to N and H at red heat; unacted on by Cl in the cold, but when heated slight explosions occur, and $CrCl_3$ and N are produced.

Chromium, oxides of. Three oxides of Cr are known, Cr_2O_3, CrO_2, and CrO_3; Cr_3O_4, Cr_5O_9, and perhaps an oxide higher than CrO_3, probably exist. Cr_2O_3 acts as a salt-forming oxide towards acids, and also shows feebly acidic properties; CrO_3 is distinctly an anhydride, it reacts with water to form the acid H_2CrO_4; with acids it forms chromic salts, CrX_3, and O; no salts corresponding to CrO_2 have been prepared, this oxide is said to evolve Cl by the action of HClAq. Chromous oxide, CrO, is not known, but approximately pure CrO H_2O (*v.* CHROMIUM, HYDROXIDES OF) has been prepared. Cr_2O_3 is said to combine directly with O to form CrO_2; it is readily oxidised in presence of alkali to chromate M_2CrO_4, from which CrO_3 is obtained. Cr_3O_4 and Cr_5O_9, if they exist, may be regarded as $CrO.Cr_2O_3$ and $2Cr_2O_3.CrO_3$, respectively; CrO_2 is sometimes regarded as $Cr_2O_3.CrO_3$ (*v.* CHROMIUM, ACIDS OF).

I. CHROMIC OXIDE Cr_2O_3 (*green oxide of chromium*). Mol. w. unknown as compound has not been gasified. S.G. 4·91 to 5·01 (Playfair a. Joule, *C. S. Mem.* 3, 57; Schröder, *P.* 106, 226). Schiff (*A.* 106, 114) gives S.G. 6·2 for crystallised Cr_2O_3. Crystallises in hexagonal forms; $a:c = 1:1·3682$. S.H. (21°–52°) ·177 (Kopp, *T.* 155, 71).

Occurrence.—As *chrome-ochre*; in combination with FeO in *chrome-ironstone.*

Formation.—1. By heating chromic hydroxide (*q. v.*).—2. By heating finely divided Cr in O. 3. By heating CrO_3.—4. By heating $(NH_4)_2Cr_2O_7$ or Hg_2CrO_4.—5. By heating $CrCl_3$ in air.

Preparation.—1. A mixture of 5 pts. finely powdered, dry, $K_2Cr_2O_7$, and 1 pt. S, is heated to redness in a crucible, and the product is washed with H_2O until all K_2SO_4 and K_2S are dissolved out (Lassaigne, *A. Ch.* [3] 14, 299; Dietrich, *W. J.* 1866. 273).—2. Equal parts of dry, powdered, $K_2Cr_2O_7$, and NH_4Cl, are mixed with a little Na_2CO_3, strongly heated so long as any gas (N) comes off, and the residue is washed free from KCl (Wöhler, *P.* 10, 46; Böttger, *A.* 47, 339).—3. *Crystalline* Cr_2O_3 may be prepared by passing vapour of CrO_2Cl_2 through a glass tube heated to low redness (Wöhler, *P.* 33, 341); or by heating to bright redness, in a Hessian crucible, a mixture of equal parts of dry, powdered, $K_2Cr_2O_7$ and NaCl, covered with a layer of NaCl, and washing the residue free from KCl and NaCl (Schiff, *A.* 106, 114; 108, 30). The crystalline oxide is also obtained by strongly heating the amorphous oxide in O (Sidot, *C. R.* 69, 201); or by fusing the amorphous oxide with $CaCO_3$ and $B\,O_3$ (Ebelmen, *A. Ch.* [3] 22, 211). Blake (*Am. S.* [2] 10, 352) found crystalline Cr_2O_3 in a furnace used for making K_2CrO_4 from chrome-ironstone. (For other methods of preparing amorphous Cr_2O_3 *v.* Barian, *A.* 40, 203; Berthier, *A. Ch.* [2] 17, 56; Böttger, *J. pr.* 103, 314. For other methods of preparing crystalline Cr_2O_3 *v.* Gentele, *J. pr.* 54, 187; Fremy, *A.* 49, 274; Muller, *P.* 127, 404; Otto, *A.* 142, 102.)

Properties and Reactions.—Amorphous Cr_2O_3 is a green powder, more or less dark, according to the method of preparation. Crystalline Cr_2O_3 forms very dark green, lustrous, hexagonal crystals; as hard as corundum; isomorphous with Fe_2O_3 and Al_2O_3. Cr_2O_3 which has been strongly heated, or crystalline Cr_2O_3, is insol. acids; fused with KNO_3, or $KHSO_4$, K_2CrO_4 is formed and dissolves in H_2O. Amorphous Cr_2O_3, if not strongly heated, dissolves in most acids to form chromic salts CrX_3. Cr_2O_3 is not reduced by H, and by C only when intimately mixed and strongly heated. Heated in Cl, CrO_2Cl_2 is formed; if the oxide is perfectly dry, a little $CrCl_3$ is produced (Moissan, *Bl.* [2] 34, 70); heated to about 410° in air, CrO_2 is produced (Moissan, *l.c.*); heated in H_2S, Cr_2S_3 results (Moissan, *l.c.*).

Combinations.—1. With *water*, indirectly, to form $Cr_2O_3.xH_2O$; *v.* CHROMIUM, HYDROXIDES OF.—2. With several *metallic oxides* to form compounds $MO.Cr_2O_3$; *v.* CHROMITES; under CHROMIUM, ACIDS OF, p. 158.

II. CHROMIUM DIOXIDE CrO_2. (*Chromium tetroxide. Brown oxide of chromium. Chromate of chromium.*) Mol. w. unknown. This oxide is a product (1) of the oxidation of Cr_2O_3, (2) of the reduction of CrO_3.

Formation.—1. By heating Cr_2O_3 in air, or O, to about 400° (Moissan, *A. Ch.* [5] 21, 243).—2. By heating $Cr_2O_3.xH_2O$ in air to about 250° (Kruger, *P.* 61, 219).—3. By the action of conc. Cr_23SO_4Aq, or $CrCl_3Aq$, on K_2CrO_4Aq

$$(?\ 5K_2CrO_4Aq + Cr_23SO_4Aq = 3K_2SO_4Aq + 2K_2Cr_2O_7Aq + 3CrO_2)$$

(Maus, *P.* 9, 127; Bensch, *P.* 55, 98).—4. By the action of $Na_2S_2O_3Aq$ on $K_2Cr_2O_7Aq$

$$(?\ 2K_2Cr_2O_7Aq + Na_2S_2O_3Aq = K_2CrO_4Aq + K_2SO_4Aq + Na_2SO_4Aq + 3CrO_2)$$

(Popp, *A.* 156, 90). (For other methods *v.* Kopp, *C. N.* 11, 16; Vogel, *J. pr.* 77, 482; Siewert, *Z. f. d. ges. Naturwiss.* 18, 285; Schiff, *A.* 120, 207; Traube, *A.* 66, 106; Rammelsberg, *A.* 60, 203; Braun, *J. pr.* 90, 356; Oppenheim, *Bl.* [3] 1, 165).

Preparation.—NO is passed into warm dilute $K_2Cr_2O_7Aq$; CrO_2 is slowly ppd.: the solution must not become concentrated $(?\ 2K_2Cr_2O_7Aq + 2NO = 2KNO_3Aq + K_2CrO_4Aq + 3CrO_2)$. The pp. is washed with H_2O, then with alcohol, and dried at 250° for a long time until the weight is constant (Schweizer, *J. pr.* 39, 269; Hintz, *A.* 169, 367).

Properties and Reactions.—Dark grey, almost black, powder; very hygroscopic. Loses O at 300°; heated in Cl to 250° a little $Cr_3O_6Cl_2$ is formed; heated with HClAq, or with mixture of HClAq and H_2SO_4Aq, evolves Cl (Moissan, *A. Ch.* [5] 21, 243); heated with KOHAq, out of contact with air, forms K_2CrO_4Aq and Cr_2O_3 (Moissan, *l.c.*); not acted on by PCl_5 (Hintz, *A.* 169, 367).

III. CHROMIUM TRIOXIDE CrO_3. (*Chromic anhydride. Red oxide of chromium.*) Mol. w. unknown. S.G. 2·67–2·82 (Playfair a. Joule, *C. S. Mem.* 3, 57; Schafarik, *Sits. W.* 47 [2nd part], 256). Crystallises in trimetric prisms; $a:b:c = {\cdot}7246:1:{\cdot}6285$. [About 190°] (Zettnow, *P.* 143, 468). S. (26°) 165 (Zettnow, *l.c.*).

Occurrence.—In combination with PbO, CuO, &c., in a few minerals.

Formation.—Chromates, M_2CrO_4, are produced by heating Cr_2O_3 with alkaline oxidisers, *e.g.* KOH, KNO_3, $KClO_3$; or by the action of oxidisers—*e.g.* Cl, $K_2Mn_2O_8$Aq—on $Cr_2O_3.xH_2O$ in KOHAq. CrO_3 is obtained from chromates by the action of strong acids.

Preparation.—300 grams commercial $K_2Cr_2O_7$ are warmed with 500 c.c. H_2O and 420 c.c. conc. H_2SO_4 until dissolved; after 10–12 hours the mother liquor is poured off from the crystals of $KHSO_4$; the solution is kept at 80°–90°, 150 c.c. conc. H_2SO_4 are added, and then H_2O drop by drop till the pp. of CrO_3 has just dissolved; the liquid is evaporated until crystallisation begins. After 10–12 hours the liquid is separated from crystals of CrO_3 by pouring through a funnel in which is placed a little filter of thin Pt pierced with small holes. The mother liquor yields a second and third crop of CrO_3 crystals, by evaporation. The crystals of CrO_3 are spread out on a porous plate, after 24 hours they are removed, 50 c.c. pure HNO_3Aq (S.G. 1·46) are added, and the whole is placed on another porous plate; if after 12 hours the CrO_3 still gives reactions for H_2SO_4 and K, 25 c.c. HNO_3Aq are added and exposure on a porous plate is repeated. The HNO_3 is now removed by warming the crystals in a basin, at first very slightly, then to a rather higher temperature (60°–80), until the crystals appear perfectly dry and fumes of HNO_3 are no longer evolved. About 84 p.c. of pure CrO_3 is obtained (Zettnow, *P.* 143, 468; modification of methods of Bolley, *A.* 56, 113, and Bunsen, *A.* 148, 289). CrO_3 may also be prepared from $PbCrO_4$ by the action of conc. H_2SO_4 (Schrötter, *P.* 59, 616); or by the action of HNO_3Aq (Duvillier, *C. R.* 75, 711); also from $BaCrO_4$ (Duvillier, *l.c.*); also by the action of moisture on a fluoride of Cr (? oxyfluoride; *v.* CHROMIUM FLUORIDE, p. 163) obtained by decomposing $PbCrO_4$ and CaF_2 by conc. H_2SO_4 (Unverdorben, *N. J. P.* 9, 26; Berzelius, *Lehrbuch* [5th ed.], 2, 319).

Properties.—Carmine-red, very lustrous, trimetric prisms (Nordenskjold, *P.* 114, 612); or loose, red, flakes. When melted at about 190° and solidified, appears as very dark red, metal-like, crystalline mass. Very sol. in H_2O; $[CrO^3, Aq] = 1{,}900$ (Sabatier, *C. R.* 103, 267); S.G. of solution containing *x* p.c. CrO_3 at temperature *t* (Zettnow, *P.* 143, 474):—

x.	*t.*	S.G.
8·25	16°	1·0606
12·34	19·5	1·0957
19·33	19	1·1569
31·83	20·1	1·2026
37·77	22	1·3441
62·23	22	1·7028

Sol. in pure ether and in cold dilute alcohol (Zettnow, *l.c.*). Solution in water is acid and reacts with metallic oxides, &c., to form salts M_2CrO_4 (*v.* CHROMIC ACID). CrO_3 is easily deoxidised; by action of acids it yields chromic salts CrX_3, and gives up O.

Reactions.—CrO_3 is very easily reduced. 1. CrO_3Aq is reduced by *hydrogen* (Ludwig, *A.* 162, 47).—2. Amorphous *phosphorus* heated to 200° forms CrO_2; P dissolves in CrO_3Aq forming an acid phosphate of Cr (Oppenheim, *Bl.* [2] 1, 165).—3. *Potassium* or *sodium* reduces CrO_3 on heating, probably to Cr.—4. *Sulphur* forms Cr_2S_3 and SO_2 (Moissan, *A. Ch.* [6] 5, 568).—5. Heated with *sulphydric acid*, Cr_2S_3, H_2O, and S are formed (Harten, *A.* 37, 350).—6. With *haloid aqueous acids*, halogen is evolved and CrX_3 formed.—7. *Sulphurous anhydride* has no action at 100°; at 180° CrO_2 and SO_3 are formed (Traube, *A.* 66, 103); SO_2Aq and CrO_3Aq form at first H_2SO_4Aq and CrO_2, and then $Cr_2 3SO_4$Aq. 8. *Nitric oxide* reduces CrO_3 to Cr_2O_3 (Reinsch, *J. pr.* 28, 391; Wöhler, *A.* 34, 236).—9. *Arsenious oxide* forms Cr_2O_3 and H_3AsO_4Aq with CrO_3Aq.—10. *Ammonia* forms Cr_2O_3, H_2O, and N; light is produced.—11. *Phosphoric chloride* forms CrO_2Cl_2 and $POCl_3$ (Schiff, *A.* 106, 116).—12. *Ferric chloride* heated with CrO_3 forms Fe_2O_3 and CrO_2Cl_2 (Geuther, *A.* 106, 239).—13. Heated with violet *chromic chloride* CrO_2Cl_2 and Cr_2O_3 are formed (Geuther, *A.* 118, 69).—14. CrO_3Aq is reduced to Cr_2O_3 by *stannous chloride*, $SnCl_4$ and SnO_2 being formed.—15. Cold conc. *sulphuric acid* dissolves CrO_3 (it is said to be quite insoluble in very conc. acid with 16–17 p.c. H_2O added); a compound $CrO_3.H_2SO_4$ is probably formed (*v. Combinations*, No. 2), but on heating, $Cr_2 3SO_4$, or a basic Cr sulphate ($4Cr_2O_3.6SO_3.7H_2SO_4$ according to Cross a. Higgins, *C. J.* 41, 113), is formed, with evolution of O.—16. CrO_3Aq is reduced by *electrolysis* to Cr, Cr_2O_3, and O; 30,225 gram-units of heat are produced (Favre, *C. R.* 73, 890 a. 936; Geuther, *A.* 99, 314; Buff, *A.* 110, 257).—17. *Iodine* dissolves in conc. CrO_3Aq; the products are uncertain (Walz, *C. N.* 26, 245).—18. *Oxygen*, *ozone*, or pure dry *chlorine*, has no action on CrO_3 (Moissan, *A. Ch.* [6] 5, 568).—19. Heated with carbon disulphide to 180° a little COS is formed (Armstrong, *B.* 2, 713).—20. Very many *carbon compounds*, *e.g.* C_2H_4, C_2H_2, C_2H_6O, $C_2H_2O_4$, $C_6H_5.CH_3$, &c., are oxidised by CrO_3Aq: a mixture of $K_2Cr_2O_7$, H_2SO_4, and H_2O is generally employed.

Combinations.—1. With *water* to form H_2CrO_4 (Moissan, *A. Ch.* [6] 5, 568; *v.* CHROMIC ACID, under CHROMIUM, ACIDS OF).—2. According to Bolley (*A.* 56, 113) CrO_3 combines with *sulphuric acid* to form $CrO_3.H_2SO_4$ (? H_2CrSO_7); it is prepared by adding crystallised CrO_3 to conc. H_2SO_4, little by little, until no more is dissolved, and after some days collecting the brown solid matter and drying on a porous plate. 3. Schröder describes a compound with *sulphuric anhydride* $CrO_3.3SO_3$ (*P.* 59, 616; *v.* also Gay-Lussac, *S.* 32, 447; Fritzsche, *J. pr.* 27, 252). 4. Moissan (*C. R.* 97, 96) says that the body produced by the action of H_2O_2Aq on CrO_3Aq, usually regarded as a higher oxide than CrO_3, is really a compound of CrO_3 and H_2O_2, viz. $CrO_3.H_2O_2$ (*v. infra*).

IV. OTHER OXIDES OF CHROMIUM.

(i) The oxide Cr_3O_4—corresponding to Fe_3O_4, Ni_3O_4, and Co_3O_4—is said to be produced by the action of air-free KOHAq on $CrCl_2$Aq, immediate washing the pp. with boiling water and drying *in vacuo*; it is scarcely soluble in acids; when heated it takes up O forming Cr_2O_3 (Péligot, *A. Ch.* [3] 12, 539). By electrolysing $CrCl_2$Aq, containing $CrCl_3$, under special conditions, Bunsen obtained a black, amorphous, powder, insol. acids, oxidised by heating in air to Cr_2O_3 (*P.* 91, 619). This powder seems to have been either a mixture or a compound of CrO and Cr_2O_3 (but *v.* Geuther, *A.* 118, 66).

(ii) When CrO_3 is heated in air, or O, to a little over 200° (Geuther a. Merz, *A.* 118, 62), or when a rapid stream of CrO_2Cl_2 vapour is passed through a tube heated to above 200°, but not to redness (Wohler, *A.* 111, 117), small, lustrous, dark-violet, trimetric prisms, S.G. about 4, are obtained. According to Wöhler the composition is Cr_3O_5; according to Geuther Cr_5O_9. These crystals are distinctly magnetic, but lose their magnetism by heating in air; when strongly heated Cr_2O_3 is formed. Insoluble in all acids including *aqua regia*; slowly acted on by conc boiling KOHAq; decomposed by molten KOH to Cr_2O_3 and K_2CrO_4.

Traube (*A.* 66, 108) describes two oxides Cr_8O_{11} and Cr_5O_{12}; but the existence of these as definite compounds is doubtful.

(iii) When H_2O_2Aq is added to CrO_3Aq, or when a dilute, strongly acid, solution of BaO_2 in HClAq is added to $K_2Cr_2O_7Aq$, a deep-blue colour is produced in the solution (Barreswill, *A. Ch.* [3] 20, 364); this colour quickly disappears, O being evolved (Schönbein, *P.* 108, 471). The blue compound is more stable in ethereal than aqueous solution. BaO_2 is added to HClAq, ether (free from alcohol) is then added, and then $K_2Cr_2O_7Aq$ drop by drop with constant shaking; the ether becomes deep azure blue, it is free from HCl and H_2SO_4. The ethereal solution evolves O when evaporated, and CrO_3 remains (Aschoff, *J. pr.* 81, 401 a. 487). Ferrous salts are oxidised by the blue ethereal liquid; alkalis decompose it to alkali chromates and O; it is also decomposed by P_2O_5, $CaCl_2$, MnO_2, Pb_3O_4, HgO, Na, and by acids and bases (Moissan, *C. R.* 97, 96; *v.* also Martinon, *Bl.* [2] 45, 862). Certain alkaloids, *e.g.* strychnine and quinine, seem to form compounds with the blue-coloured body; these compounds are, however, unstable. According to Aschoff (*J. pr.* 81, 401 a. 471), for the formation and complete decomposition of the blue-coloured compound H_2O_2 reacts with $K_2Cr_2O_7$ in the ratio $5H_2O_2:K_2Cr_2O_7$: assuming the blue compound to be an oxide of Cr with the composition Cr_2O_7, the reaction in question might be represented as
(1) $K_2Cr_2O_7Aq + H_2O_2Aq + 2HClAq =$
$2KClAq + 2H_2OAq + Cr_2O_7Aq$;
(2) $Cr_2O_7Aq + 6HClAq + 4H_2O_2Aq =$
$Cr_2Cl_6Aq + 7H_2OAq + 8O$. Fairley (*C. N.* 33, 237) supposes that the blue compound is $CrO_6.3H_2O$. Moissan (*C. R.* 97, 96) obtained an ethereal solution of the dark-blue compound containing 5 p.c. Cr; at −20° *in vacuo* deep indigo blue, oily, drops were produced; by the action of Na, H was evolved, and by gently warming O was evolved; the volumes of these gases obtained corresponded with those required by the formula $CrO_3.H_2O_2$. The blue compound cannot be obtained by the action of ozone on CrO_3Aq; it is formed during electrolysis only when H_2O_2 is also produced (Moissan, *l.c.*).

Chromium, oxychlorides of. Various oxychlorides, or perhaps compounds of Cr_2O_3 and $CrCl_3$, are obtained by evaporating $CrCl_3Aq$ at different temperatures (p. 167). Of the compounds theoretically derivable from $CrO_2(OH)_2$ by replacing OH by Cl, viz. CrO_2OHCl and CrO_2Cl_2, the second only is known; the first would react as an acid, the K salt of this acid is known (*v.* *Chloro-chromates* under CHROMIUM, ACIDS OF, p. 157). CrO_2Cl_2 easily parts with O and Cl; heated in a closed tube $Cr_3O_6Cl_2$ is produced.

I. CHROMYL CHLORIDE CrO_2Cl_2 (*Chlorochromic acid. Chlorochromic anhydride*). Mol. w. 155·06. (115·9°) (Thorpe, *C. J.* 37, 362). S.G. $^{0}_{4}$ 1·9617 (Thorpe, *l.c.*). V.D. 78.

Formation.—1. Equal parts CrO_3 and $FeCl_3$ are heated together in a retort (Geuther, *A.* 106, 239).—2. CrO_3 and $CrCl_3$ are heated together in the ratio $2CrCl_3:3CrO_3$ (Geuther, *A.* 118, 69).—3. 1 part CrO_3 and 2 parts PCl_5 are heated together (Schiff, *A.* 106, 116).—4. HCl is passed into conc H_2SO_4 containing CrO_3 in suspension (*B.* 10, 1041).—5. HCl is passed over CrO_3 (Moissan, *A. Ch.* [6] 5, 568).

Preparation.—10 parts NaCl are fused with 12½ parts $K_2Cr_2O_7$; the fused mass in fair-sized pieces is placed in a retort connected with a well-cooled condenser, and 25 parts fuming H_2SO_4 are added. The reaction proceeds without heating (Thomson, *T.* 1827. 159; Berzelius, *B. J.* 6, 131; Wöhler, *P.* 33, 343; Etard, *A. Ch.* [5] 22, 218). About 70 p.c. of the theoretical yield of CrO_2Cl_2 is obtained; part of the CrO_2Cl_2 is decomposed by the acid to CrO_3, Cl, and Cr_23SO_4 (Etard, *l.c.*). The distillate is redistilled several times in CO_2.

Properties.—A dark-red, mobile, liquid; fumes much in the air; dissolves Cl and I in large quantities. The vapour absorbs all the light from a luminous flame except a narrow band in the red (Stoney a. Reynolds, *P. M.* [4] 41, 291). If the vapour is mixed with O and passed into a Bunsen lamp a violet flame is produced, showing lines in the violet, green, yellow, orange, and red, part of the spectrum (Gottschalk a. Drechsel, *J. pr.* 89, 473). CrO_2Cl_2 is best kept in sealed glass tubes.

Reactions.—1. Easily parts with O and Cl; acts as an energetic oxidiser and chlorinating agent, *e.g.* oxidises P, S, Hg, alcohol, turpentine, &c., oxidises and chlorinates C_6H_6 (forming $C_6HCl_3O_2$), $C_{10}H_8$ (forming $C_{10}H_4Cl_2O_2$) &c. (*v.* Liebig, *P.* 21, 359; Schrötter, *A.* 37, 148; Heintze, *J. pr.* [2] 4, 211; Carstanjen, *J. pr.* [2] 2, 51).—2. Heated with PCl_3, $POCl_3$, or PCl_5, $CrCl_3$ and Cr_2O_3 are formed with evolution of Cl (Casselmann, *A.* 98, 213; Schiff, *A.* 102, 111; Weber, *P.* 107, 375; Cronander, *B.* 6, 1466). 3. With *water*, CrO_3Aq and HClAq are formed with production of much heat.—4. Decomposed, giving crystalline CrO_3, when passed through a *warm tube* (Wöhler, *P.* 33, 331).—5. Heated in a closed tube to 180°, $Cr_3O_6Cl_2$ and Cl are formed (Thorpe, *C. J.* [2] 8, 31).—6. *Iodine* dissolves in CrO_2Cl_2; on heating $Cr_3O_6Cl_2$ and ICl are formed (Macivor, *C. N.* 28, 138).—7. Reacts with KClAq to form $CrO_2.OK.Cl$ (*q. v.* under CHROMATES) and HClAq (Péligot, *A. Ch.* 52, 267).—8. With K_2CrO_4Aq combines to form $CrO_2.OK.Cl$ (Geuther, *A.* 106, 240).—9. Burns in dry NH_3 to form NH_4Cl and CrO_2 (Rideal, *C. J.* 49, 367).

II. TRICHROMYL CHLORIDE $Cr_3O_6Cl_2$ (*Chromium chromato-chloride*). Mol. w. unknown.

Formation.—1. Potassium chlorochromate,

$CrO_2OK.Cl$ is heated with conc. H_2SO_4; CrO_2Cl_2 and $Cr_3O_6Cl_2$ are produced together (Zettnow, *P.* 143, 328).—2. I is dissolved in CrO_2Cl_2, and the product is distilled (Macivor, *C. N.* 28, 138).

Preparation.—CrO_2Cl_2 is heated in a closed tube for several hours to 180°, and the residue is heated in dry CO_2 to 120° to remove unchanged CrO_2Cl_2 (Thorpe, *C. J.* [2] 8, 31).

Properties and Reactions.—A black, amorphous, very deliquescent powder; heated in air, O, Cl, and Cr_2O_3 are formed; easily reduced by H to Cr_2O_3 with evolution of O and Cl; dissolves in HClAq, Cl is evolved, and $CrCl_3Aq$ remains; aqueous solution also gives off Cl on heating.

III. Oxychlorides from $CrCl_3Aq$ (Moberg, *J. pr.* 29, 175; Lœwel, *J. pr.* 37, 38; Péligot, *J. pr.* 37, 475; Schiff, *A.* 124, 157; Ordway, *Am S.* [2] 26, 197; Béchamp, *A. Ch.* [3] 56, 306; 57, 296). By evaporating $CrCl_3Aq$ at 120° a reddish residue, soluble in H_2O, agreeing with composition $Cr_2O_3.8CrCl_3.24H_2O$, was obtained; this heated to 150° left a reddish-grey powder, $Cr_2O_3.4CrCl_3.9H_2O (= Cr_2OCl_4.3H_2O)$; when more strongly heated, and water added, a residue remained, $2Cr_2O_3.2CrCl_3 (= CrOCl)$ (Moberg). Cr_2OCl_4 was also obtained by heating $CrCl_3.xH_2O$ to 150°-260°, and by long-continued digestion of $Cr_2O_3.xH_2O$ with cold dilute HClAq (Lœwel; Péligot).

$CrOCl.3H_2O$ was obtained by adding BaO_2H_2Aq to $CrCl_3Aq$ until the pp. no longer dissolved, evaporating, treating the residue with alcohol ($BaCl_2$ remained), evaporating to dryness at 100° and drying at 120° (Péligot); the same compound was obtained by boiling $CrCl_3Aq$ with $Cr_2O_3.xH_2O$ (Béchamp).

Chromium, oxyfluoride of, CrO_2F_2. Said to be obtained by reaction between $PbCrO_4$, CaF_2, and H_2SO_4 (*v.* Oliveri, *G.* 16, 218).

Chromium, phosphide of, CrP. Mol. w. unknown. S.G. 4·68.

Formation.—1. By strongly heating $CrPO_4$ with C (H. Rose, *P.* 34, 333)—2. By passing PH_3 over hot $CrCl_3$ (H. Rose, *l.c.*).

Preparation.—Pieces of P are placed in the closed end of a tube of very infusible glass; dry K_2CrO_4 is placed at a little distance from the P. The K_2CrO_4 is heated to redness; the P is then heated so that the vapour passes over the K_2CrO_4; much heat and light are produced during the reaction. The product is treated with H_2O, which dissolves out K phosphates and leaves the CrP (Martius, *A.* 109, 82).

Properties and Reactions.—A grey-black, crystalline, metal-like powder; insoluble in all acids; heated in O, burns to $CrPO_4$; heated in Cl, forms PCl_3 and $CrCl_3$; oxidised by molten KOH with evolution of H, and by molten $KClO_3$ with evolution of Cl.

Chromium, salts of. Compounds obtained by replacing H of acids by Cr. Two series of Cr salts exist; chromous salts CrX_2, and chromic salts CrX_3, where $X = Cl$ &c., $\frac{SO_4}{2}$ &c., $\frac{PO_4}{3}$ &c. The V. D. of two compounds of Cr, viz. CrO_2Cl_2 and $CrCl_3$, have been determined; from this, and the S.H. of Cr, the value for the atomic weight of the element is found to be 52·4: the simplest formulæ that can be given to the salts of Cr (Cr = 52·4) are CrX_2 and CrX_3, but these formulæ do not necessarily represent the composition of gaseous molecules.

Chromous chloride, $CrCl_2$, is the starting-point for preparing most of the *chromous salts*; these salts are red or blue, and soluble in water; they very quickly absorb O, becoming chromic salts; they also absorb NO, and also C_2H_2 (Berthelot, *A. Ch.* [4] 9, 385). The most stable chromous salts at present known are the sulphate $CrSO_4.7H_2O$, blue crystals isomorphous with $FeSO_4.7H_2O$; the acetate $Cr(C_2H_3O_2)_2.H_2O$, red trimetric prisms; and the oxalate CrC_2O_4, yellow crystalline powder, more stable than any other chromous salt. (For more details of individual salts *v.* Acetates, Carbonates, Borates, Oxalates, Phosphates, Sulphates, Sulphites; also Chromous bromide, Chloride, Hydroxide, Sulphide.)

The normal *chromic salts*, CrX_3, are obtained by dissolving $Cr_2O_3.xH_2O$ in acids, or by double decomposition from soluble chromic salts obtained in this way; these salts may be regarded as derived from the hydroxide $Cr_2O_6H_6$. Numerous basic salts also exist, many derived from the hydroxide $Cr_2O.O_4H_4$ (*v.* Chromic hydroxides). The starting-point in the preparation of chromic salts is usually $K_2Cr_2O_7$; a solution of this salt is heated with HClAq, or H_2SO_4Aq, and a reducing agent (commonly alcohol or SO_2Aq); $CrCl_3Aq$ or Cr_23SO_4Aq is thus obtained; addition of NH_3Aq pps. $Cr_2O_3.xH_2O$, from which the chromic salts are obtained by the action of acids. Very many chromic salts exist in two forms, one violet to red, the other green. In some cases both varieties are known in the solid form and with the same composition, *e.g.* red and green Cr_23SO_4; in other cases only a violet salt is known in crystals, but a green solution is obtainable from this. Aqueous solutions of most of the violet salts when boiled become green; many of these solutions become red or violet again on cooling, sometimes only after standing a long time. Only the violet, or red, solutions yield crystalline salts; the green solutions give amorphous, gummy solids on evaporation. Various hypotheses have been suggested to account for these colour-changes. The change does not seem to be due to hydration and dehydration (Schrötter, *P.* 53, 513), as dehydrating agents do not effect the change from red to green (Doyer van Cleeff, *J. pr.* [2] 23, 58). The experiments of Kruger (*P.* 61, 218), Siewert (*A.* 126, 91), and Doyer van Cleeff (*J. pr.* [2] 23, 58) seem to show that in some cases at any rate, *e.g.* chrome-alum, the normal violet salt is partially decomposed, on boiling, into basic salt and acid, and that on cooling the normal (violet) salt is re-formed. Van Cleeff dialysed a green solution of chrome-alum, and found the dialysate to contain free H_2SO_4, and the liquid in the dialyser excess of Cr_2O_3; he also dialysed a violet solution of chrome-alum, and found the same composition in the liquid, both inside and outside the dialyser. The same chemist also found that the violet solution became green on addition of a little KOH, NaOH, NH_3, or alkaline carbonate; and that a little acid sufficed to reproduce the violet colour. For details of individual salts *v.* the arts. Carbonates, Borates, Nitrates, Sulphates, &c. &c.

Chromium, selenides of, CrSe and Cr_2Se_3. Moissan (*C. R.* 90, 817) describes these compounds as black powders; Cr_2Se_3 obtained by heating Cr_2O_3 in Se vapour, or $CrCl_3$ in H_2Se; CrSe obtained by heating Cr_2Se_3 in H, or $CrCl_2$ in H_2Se.

Chromium, sulphides of, Cr and S combine when heated together to form Cr_2S_3; the same sulphide is produced by heating Cr_2O_3, $CrCl_3$, CrO_3, &c., in H_2S. No sulphide of Cr, but only $Cr_2O_3.xH_2O$, is produced by the action of H_2S, alkali sulphides, &c., on solutions of Cr salts. Cr_2S_3 is reduced by H to CrS. The sulphide Cr_3S_4 has also been obtained. Phipson (*C. N.* 4, 125) stated that a heptasulphide Cr_2S_7 exists; but this has been disproved (*v.* Bender, *B.* 20, 756). Compounds of Cr_2S_3 with ZnS, MnS, FeS, &c., are obtained indirectly, *e.g.* $ZnS.Cr_2S_3$; Cr_2S_3 therefore resembles Cr_2O_3 inasmuch as it acts as a feebly salt-forming sulphide towards more positive sulphides.

I. CHROMIC SULPHIDE Cr_2S_3. Mol. w. unknown. S.G. 3·77 (Schafarik, *J.* 1863. 225). *Preparation.* Dry H_2S is passed over Cr_2O_3 heated to about 440°; the product is powdered and again heated in H_2S, and finally washed with H_2O, and dried at 100° (Moissan, *C. R.* 90, 817). Cr_2S_3 is also obtained by the action of H_2S on hot $CrCl_3$ (Liebig, *P.* 21, 359); or on Cr_23SO_4 (Traube, *A.* 66, 87); or by strongly heating Cr_2O_3 in CS_2 (H. Rose); or $K_2Cr_2O_7$ in CS_2 (Schafarik, *J. pr.* 90, 9; Müller, *P.* 127, 404); or by heating $Cr_2O_3.xH_2O$ with S, in absence of air (Berzelius).

Properties and Reactions.—Brown-black, lustrous powder, steel-grey if fused; not attacked by acids, except HNO_3Aq and *aqua regia*, which dissolve it. Heated in air, gives SO_2 and Cr_2O_3; in Cl, gives S_2Cl_2 and $CrCl_3$; with molten KNO_3, K_2CrO_4 and K_2SO_4 are formed; heated in H, gives off H_2S and S, and CrS remains (Moissan, *C.R.* 90, 817).

Combinations.—Cr_2S_3 is not acted on by KOHAq or K_2SAq; but by heating K_2CrO_4 with K_2CO_3 and S, and washing with water, greenish-black crystals (S.G. 2·79) are obtained, which are easily soluble in HNO_3Aq; these are probably a compound of K_2S and Cr_2S_3 (Kopp, *C. R.* 19, 1156; Schafarik, *J. pr.* 90, 9). By heating $Cr_2O_3.xH_2O$, $MO.xH_2O$ (or $M_2O_3.xH_2O$), and S, in S vapour, and then in CO_2 until no more S is given off, Gröger (*Sitz. W.* 81 [2nd part], 531) obtained compounds of the form $MS.Cr_2S_3$; M = Zn, Fe, Mn. (*v.* CHROMIUM, THIOACID OF).

II. CHROMOUS SULPHIDE CrS. Mol. w. unknown. A black powder, produced by heating Cr_2S_3 in H, or by heating $CrCl_3$ in H_2S at 440° (Moissan, *C. R.* 90, 817). Unchanged by heating in absence of air; heated in air Cr_2O_3 and SO_2 are formed; heated in Cl, gives $CrCl_3$; scarcely acted on by acids.

III. CHROMIUM TETRASULPHIDE Cr_3S_4. Mol. w. unknown. A greyish-black powder; insoluble in H_2O; slightly soluble in conc. HClAq, easily in conc. HNO_3Aq. Prepared by heating dry Cr_2O_3 thoroughly mixed with excess of well-powdered S in H until no more S is given off, again mixing with S and again heating in H (Gröger, *Sitz. W.* 81 [2nd part], 531).

Chromium, sulphocyanides of, and derivatives of these compounds, *v.* SULPHOCYANIDES, under CYANIDES

Chromium, thioacid of. No thioacid of Cr is known; but Cr_2S_3 behaves towards some more positive metallic sulphides as a salt-forming sulphide; in this respect it may be regarded as the thioanhydride of *hypothetical thiochromous acid*, $H_2Cr_2S_4$. Gröger (*Sitz. W.* 81 [2nd part], 531) obtained the thiochromites $ZnCr_2S_4$, $FeCr_2S_4$, and $MnCr_2S_4$, by heating mixtures of Cr hydroxide and hydroxide of Zn, Fe, or Mn, with S, for some time, then powdering and heating in S vapour for several hours, and finally heating in CO_2 until S was no longer given off. These thiochromites are dark-brown or black powders, insoluble in H_2O and HClAq, soluble in HNO_3Aq and *aqua regia*. M. M. P. M.

CHROMIUM GROUP OF ELEMENTS. *Chromium, Molybdenum, Tungsten, Uranium.*—These four metals were discovered towards the end of the eighteenth century. None of them is found in the free state in nature, and the minerals in which their salts occur are all comparatively rare. Chromium was obtained in 1797 by Vauquelin from a mineral now known to consist chiefly of lead chromate; in 1782 Hjelm prepared molybdenum from an acid earth-like compound, which Scheele had obtained four years earlier from molybdenum-glance, a substance until then supposed to be the same as galena; three years after the preparation of molybdenum a new metal was obtained by the brothers d'Elhuyar, by deoxidising an acid which they had prepared from the mineral wolframite. This acid was shown to be identical with that which Scheele had made in 1781 from the Swedish mineral tungstein, hence the new metal was called tungsten, or by some chemists wolfram. Uranium was the name given by Klaproth to a new metal obtained by him 1789 from pitchblende.

Chromium, molybdenum, and tungsten are obtained by reducing the oxides of these metals by carbon at a high temperature; uranium is prepared by removing chlorine from the chloride by means of sodium. These metals are very hard and very infusible; uranium is fairly malleable; the others are brittle. The table on p. 169 presents the prominent physical and chemical properties of the chromium metals.

General formulæ and character of salts.

MO, M_2O_3, MO_2, MO_3; MS, M_2S_3, MS_2, MS_3, MS_4; MCl_2, MCl_3, MCl_4, MCl_5, MCl_6; H_2MO_4, $H_2M_2O_7$, &c. The lowest oxides, MO, are scarcely known; hydrates of these oxides, when M = Cr or Mo, appear to exist; a few chromous salts, *e.g.* $CrSO_4 7H_2O$, exist, but are unstable, and easily become chromic salts. Sesquioxides, M_2O_3, of Cr and Mo are known; the former dissolves in acids with production of well-marked salts, the chromic salts, Cr_23SO_4, Cr_26NO_3, Cr_22PO_4, &c.; the latter is easily oxidised to MoO_2, when moist it dissolves in acids, but no definite salts have been obtained from such solutions. Dioxides, MO_2, of all the metals of the group have been prepared: of these, CrO_2 is the least stable towards heat or the action of acids, it parts with oxygen at 300°, and dissolves in acids apparently without deoxidation, but without producing definite salts; MoO_2 and WO_2 also dissolve in acids and produce salts, which, however, have scarcely been obtained in definite crystalline form; the solutions of MoO_2 readily take up oxygen from the air; both oxides, when heated, are oxidised to MO_3; UO_2 dissolves in acids to form a series of uranous salts, *e.g.* $U(SO_4)_2$, which are fairly easily oxidised to uranyl salts, *e.g.* UO_2SO_4; when this oxide is heated it becomes U_3O_8. The oxides MO_3 are all anhydrides; the mono-hydrated oxides $MO_3H_2O(=H_2MO_4)$ act as dibasic acids, forming salts X_2MO_4; several series of salts derived from more complex hydrates of MO_3 are also known, *e.g.* $X_2M_2O_7$, $X_2M_3O_{10}$, $X_2M_4O_{13}$, &c., in the case of each metal except Cr these di- tri- or tetra-salts are more distinctly marked than the salts X_2MO_4. The anhydride CrO_3 combines with some normal salts, *e.g.* $K_2CrO_4CrO_3$, and also with a few anhydrides, *e.g.* $CrO_3.3SO_3$; when dissolved in warm acids it forms chromic salts (Cr_23SO_4, &c.) with evolution of oxygen. The anhydrides MoO_3 and WO_3 form a series of complex compounds with anhydrides and water; *e.g.*

$P_2O_5.20MoO_3.38H_2O$; $SiO_2.12MoO_3.26H_2O$; $P_2O_5.24WO_3.6H_2O$; $P_2O_5.22WO_3.6H_2O$, &c. &c.;

MoO_3 also combines with SO_3 to form MoO_3SO_3 (? MoO_2SO_4). The anhydride UO_3 dissolves in acids to form uranyl salts, *e.g.* UO_2SO_4, $UO_2(NO_3)_2$, &c., which are more stable than the uranous salts derived from UO_2. The metals of the chromium group form several other oxides intermediate between those briefly described, *e.g.* Cr_5O_9 intermediate between Cr_2O_3 and CrO_2, W_3O_8 and W_4O_{11} between WO_2 and WO_3, U_2O_5 and U_3O_8 between UO_2 and UO_3: there are also indications of the existence of a more oxidised oxide than CrO_3

	CHROMIUM.	MOLYBDENUM.	TUNGSTEN.	URANIUM.
Atomic Weights.	52·4.	95·9.	183·6.	239.
	One or more compounds of each element have been gasified; specific heats have been directly determined. Molecular weights unknown.			
Melting points.	Above m.p. of Pt (which is 2000°–2500°).	Infusible at full white heat.	Softens and agglomerates at white heat.	A full red-heat.
Spec. grav. (approx.).	6·5–6·8.	8·5–8·6.	18·2–19·2.	18·4–18·7.
Specific heats.	0·10 (? too low).	0·066	0·0334.	0·028.
Atom. weight. / Spec. grav. (approx.).	7·7.	11·3.	9·7.	12·9.
Occurrence and preparation.	Occurs chiefly as chrome - ironstone, $FeO.Cr_2O_3$, in which FeO is more or less replaced by MgO &c., and Cr_2O_3 by Al_2O_3 &c.; also as lead chromate, &c.; not widely diffused; obtained by deoxidising Cr_2O_3 by C, or removing Cl from $CrCl_3$ by means of K or Zn, or by electrolysing a solution of $CrCl_2$ containing $CrCl_3$.	Occurs in small quantities as oxide and sulphide, also as lead or cobalt molybdate; obtained by reducing the oxide or chloride by H, or the oxide by C or by KCN.	Occurs very sparingly as tungstate of Ca, of Fe and Mn, and of Pb, also as oxide; obtained by reducing the oxide or chloride in hydrogen.	Sparingly distributed as oxide in pitchblende, as uranite of Ca and of Cu, as carbonate of U and Ca &c.; obtained by reducing the chloride by means of sodium
Physical properties.	Very hard; brittle; crystalline powder composed of small, brilliant, tin-white crystals (? rhombohedra); descriptions of properties differ considerably, probably the metal has not been obtained in approximate purity.	Ashen-grey powder, or, when compressed, a silver-like, lustrous, hard, brittle, infusible metal.	Resembles iron in colour and lustre; very hard, and brittle; also obtained as a brown amorphous powder; forms a very hard durable alloy with iron.	White, lustrous; hard, softer than steel; somewhat malleable, but cannot be beaten into thin plates; also obtained as a grey - black powder

TABLE—*cont.*

	CHROMIUM.	MOLYBDENUM.	TUNGSTEN.	URANIUM.
Chemical properties.	Burns in stream of O; somewhat more stable in air than iron; heated in air becomes covered with very thin film of oxide; oxidised by molten KNO_3 or $KClO_3$, but not by molten Na_2CO_3; easily dissolved by dilute HClAq or H_2SO_4Aq, but not attacked by hot concentrated HNO_3Aq; combines easily with Cl and I when heated; decomposes steam slightly at a red heat; forms a well-marked cyanide $CrCy_3$. Replaces H of acids forming two series of salts; trioxide acts as an anhydride, forming chromic acid H_2CrO_4, from which many salts are obtained; Cr_2O_3 also forms salts (chromites) by heating with ZnO, &c. Atom of Cr is trivalent in $CrCl_3$.	Not oxidised in air at ordinary temperature, but burns at low red heat; unacted on by HCl, HF, or dilute H_2SO_4Aq; dissolves in conc. H_2SO_4; oxidised to MoO_3 by HNO_3Aq; oxidised by molten KOH, but not attacked by hot KOHAq; combines with Cl to form $MoCl_5$ when heated; also with Br to form $MoBr_2$ and $MoBr_4$, but not with I; forms a nitride (? Mo_3N_2) when $MoCl_5$ is strongly heated in NH_3. Salts in which H of acid is replaced by Mo scarcely known; MoO_3 acts as anhydride of H_2MoO_4, from which acid several series of salts are obtained; MoO_3 also combines with acid radicles, *e.g.* SO_3, P_2O_5, &c. Forms many oxyhaloid salts. Atom of Mo pentavalent.	Unchanged in ordinary air, but burns in air at red heat; combines with Cl only at a high temperature, to form WCl_6; dissolves in boiling conc. KOHAq to form K tungstate with production of H; oxidised to WO_3 by hot HNO_3Aq, H_2SO_4Aq, or HClAq; forms a nitridamide, $W_2N_2.W2NH_2$, by heating WCl_6 in NH_3. Does not appear to form salts by replacing H of acids; WO_3 is the anhydride of the acid H_2WO_4, which yields several series of salts; WO_3 also combines with acid radicles, *e.g.* SO_3, SiO_2, &c. Forms many oxyhaloid salts. Atom of W penta- and hexa-valent.	Slowly tarnishes in air; oxidised at 150°–200° in air, with evolution of light and sparks; combines with Cl or Br when heated to form UCl_4 and UBr_4; very slightly attacked by iodine vapour; heated in S vapour forms US_2; dissolves in warm dilute H_2SO_4Aq, with evolution of H, easily in HClAq, also in HNO_3Aq (when melted and cooled it is nearly insoluble in HNO_3); does not decompose water; a nitride (? U_3N_4) formed by heating UCl_4 mixed with NH_4Cl in NH_3. Forms two series of salts, uranous, *e.g.* $U(SO_4)_2$, and uranyl, salts, *e.g.* $UO_2(SO_4)$; UO_3 is the anhydride of H_2UO_4, from which several salts are derived, the most marked being $M_2U_2O_7$. Atom of U tetravalent.

(? Cr_2O_7), and the oxide UO_4 is said to have been obtained in the hydrated state.

The sulphides MS_3 (M = Mo, W) are acidic; sulpho-salts of the form H_2MS_4 are known.

Of the haloid compounds of these metals the following have been obtained as gases: $CrCl_3$, $MoCl_5$, WCl_5, WCl_6, UCl_4, UBr_4; the formulæ of these compounds represent the relative masses of their molecules. It is said that CrF_6 has also been prepared in the state of gas, but the evidence is very doubtful; the oxychloride CrO_2Cl_2 is an easily gasifiable body. Of the haloid compounds, $CrCl_3$ and UCl_5 are obtained by heating a mixture of Cr_2O_3 and C, or of UO_2 and C, in a stream of Cl gas; the former compound is very stable, the latter is reduced by strongly heating to UCl_4, which is again reduced to UCl_3 by heating in hydrogen. When Mo or W is heated in chlorine, in the one case $MoCl_5$ and the other case WCl_6 is produced, the other chlorides are obtained by heating these in H or in CO_2. All the metals of this group readily form oxyhaloid salts.

Chromic chloride is a particularly interesting compound; it exists in two varieties, one (green) soluble in water and scarcely crystallisable, the other (violet) obtainable in well-formed crystals, but with difficulty soluble in water; some other chromic salts seem also to exist in two varieties, *e.g.* the sulphate $Cr_2 3SO_4$ (*v.* CHROMIUM, CHLORIDES OF, p. 162). At least seven series of double compounds exist containing chromium, ammonia, and acid radicle (CHROMIUM, AMMONIO-SALTS OF, p. 158).

Of the four elements under consideration only Cr and U form well-marked salts by replacing the hydrogen of acids; these salts are not, however, analogous in composition or properties. The chromic salts are for the most part isomorphous with the salts of aluminium and the persalts of iron; the composition of these three groups of salts is also similar, *e.g.* $M_2 3SO_4$ where M = Cr, Al, or Fe. The uranyl salts – UO_2SO_4, &c. – to a certain extent stand by themselves, although we know of many so-called basic salts of chromium, iron, copper, &c., which resemble the uranyl salts in containing oxygen as well as metal and acid radicle.

Of the trioxides, MO_3, it may certainly be said that the most acidic in character is CrO_3, and the least acidic is UO_3; this is in accordance with the general rule that the higher oxides of the elements in the same *group* (as *group* is used in the nomenclature of the periodic law) become less acid in character as the group is ascended.

The four elements all show distinct analogies with S, Se, and Te, which occur in the same *group* but in odd *series*; *e.g.* existence of acids $MO_2(OH)_2$, and of anhydrides MO_3, &c.; but these three elements are more distinctly nonmetallic in their properties than Cr, Mo, W, or U. The elements of the chromium group, as well as the three elements S, Se, and Te, show analogies with that element which is the first *odd series* member of the group, *viz.*, oxygen (*v.* CLASSIFICATION, p. 207; also OXYGEN GROUP OF ELEMENTS. For detailed accounts of the properties of the elements of this group and their chief compounds *v.* CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM, and for the other salts of these metals, *v.* CARBONATES, NITRATES, SULPHATES, &c. M. M. P. M.

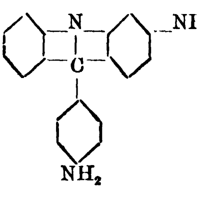
CHROMYL CHLORIDE CrO_2Cl_2 *v.* CHROMIUM, OXYCHLORIDES OF, p. 166.

CHRUSOCREATININE $C_5H_8N_4O$. A feebly alkaline substance said to occur in muscular tissue (Gautier, *Bl.* [2] 48, 18). Its solutions are ppd. by $HgCl_2$, by $ZnCl_2$, by iodine dissolved in aqueous KI, and by sodium phosphomolybdate. It forms a deliquescent hydrochloride and a crystalline platinochloride.

CHRYSAMMIDIC ACID *v.* TETRA-NITRO-OXY-AMIDO-ANTHRAQUINONE.

CHRYSAMMIC ACID *v.* TETRA-NITRO-DI-OXY-ANTHRAQUINONE.

CHRYSANILINE $C_{19}H_{15}N_3$ *i.e.*



Di-amido-phenyl-acridine.

[267°- 270°]. A by-product in the manufacture of rosaniline. Discovered by E. C. Nicholson and investigated by Hofmann (*C. R.* 55, 817; *B.* 2, 379), who prepared methyl ethyl and phenyl derivatives.

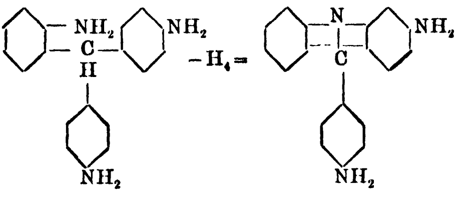
Preparation. — Commercial 'phosphine,' which is chrysaniline nitrate, is dissolved in hot water, cooled, and slowly added to dilute NaOH. The base separates as a bright yellow flocculent pp. It is dried at 100° and crystallised from benzene, which retains homologues in the mother liquid (O. Fischer a. G. Korner, *A.* 226, 177; *B.* 17, 203).

Synthesis.—By oxidising *opp*-tri-amido-triphenyl-methane $[2:1]NH_2.C_6H_4.CH(C_6H_4.NH_2[4:1])_2$, which is obtained by reduction of the product of condensation of *o*-nitro-benzoic aldehyde with aniline.

Properties.—Golden plates (from benzene) $C_{19}H_{15}N_3,C_6H_6$. The benzene of crystallisation is easily expelled. Golden needles of $C_{19}H_{15}N_3$ 2aq (from alcohol). Much less soluble in alcohol than its homologues. When pure it does not clot together when heated with NaOH. In small quantities it may be distilled without decomposition. It dyes wool and silk yellow.

Reactions. — 1. Heated with conc. HCl (8 vols.) at 170°, NH_2 is exchanged for OH and, on cooling, large red prisms of the hydrochloride of chrysophenol separate. These dissolve in NaOHAq, but on exactly neutralising, chrysophenol $C_{19}H_{14}N_2O$, separates as an orange pp., sl. sol. water, ether, or benzene, but v. sol. alcohol. From dilute alcohol it crystallises with 2aq. It is a yellow dye and a strong base, forming acid and neutral salts. It is insol. aqueous Na_2CO_3, but sol. aqueous NaOH (O. Fischer a. G. Körner, *A.* 226, 181).—2. By diazotisation and treatment with alcohol it is converted into phenyl-acridine. Chrysaniline (10 g.) dissolved in H_2SO_4 (50 g.) and water (4 g.) is well cooled and treated with nitrous acid gas in excess. The product (containing the diazo-sulphate) is slowly poured into boiling alcohol (600 g.). The alcohol is distilled off and the residue mixed with water and distilled with steam at 200°-250°. Phenyl-acridine [181°] passes over. 3g. pure chrysaniline gave 1 g. phenyl-acridine, or 40 p.c. of the theoretical yield.—3. MeI gives $C_{20}H_{16}Me_3N_3I_2$, which separates from water in red needles. NH_3 converts it into $C_{20}H_{15}Me_3N_3I$, whence Ag_2O forms $C_{20}H_{14}Me_3N_3$, a brown amorphous powder. EtI acts in the same way.

Formation in the rosaniline melt: This can be explained by two hypotheses: (1) That in the condensation of *p*-toluidine (1 mol.) with 2 mols. of aniline, together with the ordinary para-condensation producing rosaniline, a condensation simultaneously takes place which is partly ortho and produces *o*-di-*p*-tri-amido-methane, which by further oxidation yields chrysaniline—



(2) That *o*-di-*p*-tri-amido-methane is produced by condensation of 1 mol. of *o*-toluidine with 2 mols. of aniline. This latter hypothesis is the most probable and is supported by the above-mentioned synthesis (Fischer a. Körner, *B.* 17, 203).

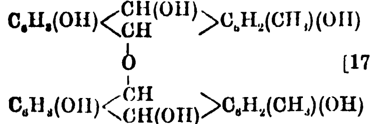
Salts. — B'2HCl. — B'2HCl aq. — B'HCl. — $B'HNO_3$.—$B'2HNO_3$.

Picric acid compound $B'(C_6H_2(NO_2)_3OH)_2$ aq (at 100°). Red needles.

Di-acetyl-derivative $C_{19}H_{11}N(NHAc)_2$.— Microscopic needles, dissolves in alcohol with a blue fluorescence, nearly insol. water. It is nearly as strong a base as chrysaniline itself and forms salts which greatly resemble the corresponding salts of chrysaniline.—B'HCl: soluble yellow microscopic needles, dyes wool and silk yellow. — $B'HNO_3$: sparingly soluble crystalline pp. (Anschütz, *B.* 17, 433).

CHRYSANISIC ACID *v.* DI-NITRO-AMIDO-BENZOIC ACID.

CHRYSAROBIN $C_{30}H_{26}O_7$ *i.e.*



$$\begin{array}{l} C_6H_3(OH)<\begin{matrix}CH(OH)\\CH\end{matrix}>C_6H_2(CH_3)(OH) \\ \qquad\qquad\quad | \\ \qquad\qquad\quad O \\ \qquad\qquad\quad | \\ C_6H_3(OH)<\begin{matrix}CH\\CH(OH)\end{matrix}>C_6H_2(CH_3)(OH) \end{array}$$

[170°–178°].

Occurs in Goa powder (also called arrarobo powder) to the extent of about 70 p.c., from which it is extracted with C_6H_6. Small yellow leaflets, m. sol. benzene, $CHCl_3$, and acetic acid, sl. sol. alcohol or ether, insol. water. Insol. NH_3Aq (difference from chrysophanic acid). By leading air into the solution in KOH, chrysophanic acid is formed: $C_{30}H_{26}O_7 + 2O_2 = 2C_{15}H_{10}O_4 + 3H_2O$. By distillation with zinc dust it yields methylanthracene.

Di-acetyl derivative. Light yellow leaflets.

Tetra-acetyl derivative [228°–230°]. Yellowish prisms; sl. sol. alcohol with a blue fluorescence. By oxidation with CrO_3 it gives di-acetyl-chrysophanic acid (Liebermann a. Seidler, *B.* 11, 1603; *A.* 212, 29; *cf.* De Silva, *Ph.* [3] 5, 723; Holmes, *Ph.* [3] 5, 801).

CHRYSATIC ACID $C_{21}H_{20}N_6O_{19}$ (Mulder, *J. pr.* 48, 16; *A.* 72, 289) or $C_{10}H_{12}N_4O_9$ (Schunck, *A.* 65, 240). An acid obtained by heating chrysammic acid with aqueous KOH. Sol. water.

CHRYSATROPIC ACID $C_{12}H_{10}O_5$. [202°]. S. (hot water) 1·3. An acid extracted by ether from an acidified infusion of the root or leaves of *Atropa belladonna* (Kunz, *Ar. Ph.* [3] 23, 722). Pale yellow trimetric prisms; may be sublimed. Sl. sol. cold water. Its alcoholic solutions exhibit green fluorescence.

CHRYSAZIN *v.* DI-OXY-ANTHRAQUINONE.

CHRYSAZOL *v.* DI-OXY-ANTHRACENE.

CHRYSENE $C_{18}H_{12}$ *i.e.*

$$\begin{array}{l} C_{10}H_6.CH \\ |\qquad\quad | \\ C_6H_4.CH \end{array}$$

. Mol. w. 228. [250°]. (above 360°). S. (alcohol) ·097 at 16°; ·17 at 78°; S. (toluene) ·24 at 18°; 5·39 at 100° (Bechi, *B.* 12, 1978). V.D. 7·95 (calc. 7·89).

Occurrence.—In coal-tar, in petroleum, and in the product of the dry distillation of fats, fir-wood, amber, and resins (Laurent, *A. Ch.* [2] 66, 136; Berthelot, *Bl.* [2] 7, 30; *J.* 1867, 605; Pelletier a. Walter, *A.* 48, 345; Williams, *J. pr.* 67, 248; Adler, *B.* 12, 1891; Prunier, *A. Ch.* [5] 17, 5).

Formation.—1. By passing naphthyl-phenyl-ethane through a red-hot tube (Graebe a. Bungener, *B.* 12, 1079).—2. The statement that chrysene is among the products of the passage of benzene through a red-hot tube has been contradicted (Berthelot, *J.* 1867, 605; *Bl.* [2] 7, 30; 22, 437; G. Schultz, *B.* 6, 415).—3. Among the products obtained by passing benzene-azo-benzene through a red-hot tube (Claus a. Suckert, *B.* 8, 37).

Properties.—Colourless scales or flat trimetric octahedra (from benzene); $a:b:c = 1:1{\cdot}376:2{\cdot}490$; v. sl. sol. alcohol, sl. sol. ether and cold CS_2, m. sol. boiling benzene and HOAc. The solutions as well as the crystals exhibit deep reddish-violet fluorescence. Hot conc. H_2SO_4 forms a blue solution (Liebermann, *A.* 158, 299). CrO_3 in HOAc gives chrysoquinone (*q.v.*). By exhaustive chlorination with $SbCl_5$ it yields CCl_4, C_2Cl_6 and per-chloro-benzene (Merz a. Weith, *B.* 16, 2881).

Picric acid compound $C_{18}H_{12}C_6H_2(NO_2)_3OH$. Reddish-brown needles (from crude xylene) (Galletly, *C. N.* 10, 243). Decomposed by alcohol.

Di-nitro-anthroquinone compound $C_{18}H_{12}C_{14}H_6(NO_2)_2O_2$. [294°]. Formed by dissolving greenish-yellow commercial anthracene [208°] (50g.) in alcohol (5 litres) and adding HNO_3 (30g. of S.G. 1·4), and boiling. Red needles; v. sl. sol. alcohol, ether, and benzene. Tin and HCl reduce the di-nitro-anthraquinone, setting free pure chrysene, which may conveniently be prepared in this way.

Di-chloro-chrysene $C_{18}H_{10}Cl_2$. [267°]. From chrysene and Cl. Soft white needles (from benzene); v. sl. sol. alcohol; may be sublimed.

Tri-chloro-chrysene $C_{18}H_9Cl_3$. [above 300°]. Slender needles (from benzene). From chrysene and Cl at 170° (Schmidt, *J. pr.* [2] 9, 270).

Di-bromo-chrysene $C_{18}H_{10}Br_2$. [273°]. From Br and chrysene in CS_2. White needles (from benzene); v. sl. sol. all menstrua. Not attacked by alcoholic KOH below 180°. $K_2Cr_2O_7$ and H_2SO_4 oxidise it to chrysoquinone.

Nitro-chrysene $C_{18}H_{11}NO_2$. From chrysene and HNO_3 (S.G. 1·25) at 100°. [209°]. Thick prisms, grouped in stars (from benzene). May be sublimed; v. sl. sol. alcohol, ether, and CS_2.

Di-nitro-chrysene $C_{18}H_{10}(NO_2)_2$. [above 300°]. From chrysene and boiling HNO_3 (S.G. 1·3). Slender yellow needles (from HOAc). V. sl. sol. alcohol, ether, and benzene.

Tetra-nitro-chrysene $C_{18}H_8(NO_2)_4$. [above 300°]. From the preceding and fuming HNO_3. Yellow needles (from HOAc). Detonates above 300°.

Tri-bromo-di-nitro-chrysene $C_{18}H_7(NO_2)_2Br_3$. Yellowish-red needles. Sol. hot alcohol, less in C_6H_6 and ether. Prepared by the action of bromine on tetra-nitro-chrysene (Adler, *B.* 12 1894).

Isomeride of chrysene $C_{18}H_{12}$. [196]. A by product in the preparation of diphenyl by action of sodium on bromo-benzene (Schultz, *A.* 174, 229). Long needles (from alcohol). Is perhaps triphenylene (Schmidt a. Schultz, *A.* 203, 135).

Isomeride of chrysene (?) $C_{18}H_{12}$. [186°]. A product of the action of Al_2Cl_6 on a mixture of naphthalene and phthalic anhydride (Ador a. Crafts, *C. R.* 88, 1355). Laminæ (from ether-alcohol). Its bromo-derivative melts at 112°.

CHRYSEUDIENE. A hydrocarbon, obtained in small quantity in the distillation of aluminum (*β*)-naphthol (Gladstone a. Tribe, *C. J.* 41, 16).

CHRYSIN $C_{15}H_{10}O_4$. *Chrysinic acid.* [275°]. S. (cold alcohol) ·66; (hot alcohol) 2. Occurs in the buds of *Populus nigra*, *P. pyramidalis*, and *P. balsamifera* (Piccard, *B.* 6, 884; 7, 888; 10, 176). The alcoholic extract, after successive treatment with lead acetate and H_2S, is evaporated, and the residue recrystallised from spirit and washed with alcohol, ether, CS_2, boiling water, and boiling benzene. The residue is heated to 275°, and crystallised from spirit. Bright yellow plates. Insol. water, nearly insol. benzene, CS_2, and chloroform. Aqueous alkalis form a yellow solution, but on boiling they split it up into phloroglucin, acetophenone, benzoic acid, and acetic acid. Lead acetate gives, in alcoholic solutions, a pp. soluble in excess.

Fe_2Cl_6 gives a violet colour in alcoholic solution.

Di-bromo-chrysin $C_{15}H_8Br_2O_4$. Formed by adding Br to an alcoholic solution of chrysin. Felted mass of silky needles.

Di-chloro-chrysin. Needles.

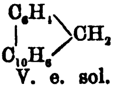
Di-iodo-chrysin $C_{15}H_8I_2O_4$. Formed by adding iodine and iodic acid to an alcoholic solution of chrysin.

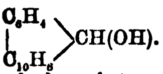
Di-nitro-chrysin $C_{15}H_8(NO_2)_2O_4$. From chrysin and HNO_3. Large crystals (from hot HOAc or aniline). Forms an orange-red basic ammonium salt and a yellow acid ammonium salt.

Methyl derivative $C_{15}H_9MeO_4$. *Tecto-chrysin.* [164°]. From chrysin, MeI, and KOH dissolved in MeOH. Exists in poplar-buds together with chrysin, from which it may be separated by means of its much greater solubility in benzene and chloroform. It is much less soluble in alcohol than chrysin. Large sulphur-yellow monoclinic prisms (from alcohol); *a:b:c* = 1·54:1:1·86; $\beta = 53°$. Insol. alkalis. It forms a di-bromo-derivative.

Ethyl derivative $C_{15}H_9EtO_4$. [146°].

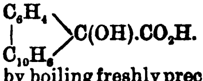
Iso-amyl derivative $C_{15}H_9(C_5H_{11})O_4$. [125°]. Its di-bromo- derivative crystallises in needles.

CHRYSOFLUORENE $C_{17}H_{12}$ *i.e.*  [188°]. Silvery glistening tables. V. e. sol. ether, chloroform, and benzene, less sol. cold alcohol. Formed by heating chrysoketone with HI and P at 150°–160° (Bamberger a. Kranzfeld, *B.* 18, 1934).

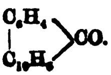
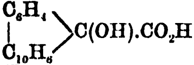
Chrysofluorene alcohol  [167°]. Formed by reduction of chrysoketone with zinc and HCl (B. a. K.). White silky needles or glistening plates. Sublimable. V. sol. alcohol. ether, and benzene, sl. sol. ligroin. Its alcoholic solution is turned blue by addition of H_2SO_4. Strong H_2SO_4 dissolves it with a reddish-violet colour.

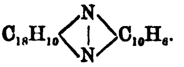
CHRYSOGEN C. 94·3 to 95 p.c.; H 5·7 to 5 p.c. [280°–290°]. S. (cold benzene) ·04; (boiling benzene) ·2; S. (boiling HOAc) ·05; (cold HOAc) ·01. An orange-coloured hydrocarbon contained in small quantity in crude anthracene, and separated therefrom by repeated crystallisation from benzene (Fritzsche, *C. R.* 54, 910; *Bl.* [2] 6, 474; Prunier, *Bl.* [2] 31, 293). Orange tables with green lustre; may be sublimed. Conc. H_2SO_4 dissolves it without change. Small quantities colour white hydrocarbons yellow. Its solution is bleached by sunlight. It forms, with di-nitro-anthraquinone, a compound crystallising in olive needles with golden lustre.

CHRYSOGLYCOLLIC ACID

 White powder. Formed by boiling freshly precipitated amorphous chrysoquinone with alkalis (Bamberger a. Kranzfeld, *B.* 18, 1933).

CHRYSOIDINE *v.* *Benzene-azo-m-phenylene diamine.*

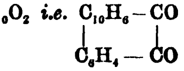
CHRYSOKETONE  [180°]. Glistening red needles. Scarcely volatile with steam. V. sol. the ordinary solvents. Formed by the oxidation of chrysoglycollic acid  with $K_2Cr_2O_7$ and H_2SO_4 (Bamberger a. Kranzfeld, *B.* 18, 1933).

CHRYSO-NAPHTHAZINE $C_{28}H_{16}N_2$ *i.e.*  Formed by mixing a solution of chrysoquinone in aqueous-alcoholic $NaHSO_3$ with an aqueous solution of naphthylene-*o*-diamine hydrochloride, sodium acetate, and acetic acid. Yellow microcrystalline powder (Liebermann a. Witt, *B.* 20, 2443).

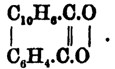
CHRYSOPHANIC ACID *v.* DI-OXY-METHYL-ANTHRAQUINONE.

CHRYSOPHANIN. A white amorphous substance said to be contained in the aqueous decoction of senna leaves (Bourgoin, *C. R.* 73, 1449).

CHRYSOPHENOL $C_{19}H_{15}N_2O$. *Oxy-amido-phenyl-acridine.* Formed by heating chrysaniline with HCl under pressure at 180°, NH_2 being replaced by OH (Fischer a. Körner, *B.* 17, 205). Small yellowish-red needles (containing aq). Sl. sol. water, benzene, and ether, v. sol. alcohol and caustic alkalis. The hydrochloride and sulphate form sparingly soluble yellow crystals.

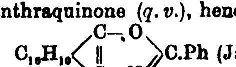
CHRYSOQUINONE $C_{18}H_{10}O_2$ *i.e.* 

$$\begin{array}{l}C_{10}H_6-CO\\ \quad\ |\qquad\quad |\\ C_6H_4-CO\end{array}$$

or 

$$\begin{array}{l}C_{10}H_6.C.O\\ |\qquad\ \ \|\ \ |\\ C_6H_4.C.O\end{array}$$

. Mol. w. 258. [235°]. Occurs in American petroleum to which, according to Prunier (*Bl.* [2] 31, 293), it imparts the blue fluorescence. Obtained by oxidising chrysene with CrO_3 in HOAc (Liebermann, *A.* 158, 309; Graebe, *B.* 7, 782; E. Schmidt, *J. pr.* [2] 9, 250, 270). Orange plates (from alcohol); m. sol. benzene and HOAc, sl. sol. ether and CS_2. May be sublimed. Conc. H_2SO_4 forms a deep-blue solution whence it is ppd. unaltered by water. $NaHSO_3$ forms a crystalline compound, decomposed by much water.

Reactions.—1. $KMnO_4$ gives phthalic acid (Anschütz a. Japp, *B.* 11, 211). -2. Distillation over *zinc-dust* forms chrysene.—3. Aqueous SO_2 at 100° forms hydro-chrysoquinone. This body is also formed by the action of zinc-dust and aqueous KOH. It is an amorphous white powder, re-oxidised by air at 200°, or by shaking its solution in H_2SO_4 with air.—4. PCl_5 and $POCl_3$ at 200° form di-chloro-chrysoquinone and deca-chloro-chrysene.—5. Distillation with *soda-lime* gives a hydrocarbon $C_{16}H_{12}$ (? phenyl-naphthalene).—6. Heated with *benzoic aldehyde* and aqueous NH_3 in sealed tubes at 100° it forms a product which, if boiled first with alcohol and then with benzene, yields to the latter a body $C_{25}H_{15}NO$ crystallising in silky needles [259°–265°] which may be sublimed. The reaction is analogous to that of benzoic aldehyde and ammonia on phenanthraquinone (*q.v.*), hence this body should be  (Japp a. Streatfeild, *C. J.* 41, 157).

Di-chloro-chrysoquinone $C_{18}H_8Cl_2O_2$. From chrysene $POCl_3$ and PCl_5 (2 mols.) at 200°; a yellow flocculent pp. is then obtained by adding alcohol (L.).

Di-bromo-chrysoquinone $C_{18}H_8Br_2O_2$. Red leaflets. [160°–165°]. Prepared by bromination of chrysoquinone (Adler, *B.* 12, 1893).

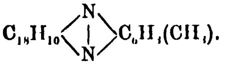
Di-nitro-chrysoquinone $C_{18}H_8(NO_2)_2O_2$. [230°]. From chrysoquinone and HNO_3 (S.G. 1·4) (A.). Red needles.

Tetra-nitro-chrysoquinone $C_{18}H_6(NO_2)_4O_2$. From chrysoquinone and cold conc. HNO_3. Orange powder (L.).

Chrysoquinone di-sulphonic acid $C_{18}H_8(SO_3H)_2O_2$.—BaA″ (A.).

Di-oxy-chrysoquinone $C_{18}H_8(OH)_2O_2$. *Chrysezarin.* [above 300°]. Said to have been extracted from crude artificial alizarin (Claus, *B.* 8, 157). Dark brown needles with bronze lustre (from HOAc). Insol. cold water, sol. alcohol, ether, and alkalis.

CHRYSO-TOLU-AZINE $C_{25}H_{16}N_2$ *i.e.*



Prepared by mixing a solution of chrysoquinone in aqueous-alcoholic $NaHSO_3$, with an aqueous solution of tolylene-*o*-diamine hydrochloride, sodium acetate, and acetic acid. Small golden needles. Sublimable. Dissolves in conc. H_2SO_4 with a blackish-violet colour (Liebermann a. Witt, *B.* 20, 2443).

CHRYSOTOLUIDINE $C_{21}H_{21}N_3$ (?). Found among the by-products in the preparation of rosaniline (De Laire, Girard, a. Chapoteaut, *C. R.* 63, 964).

CICUTA OIL. The oil from the seeds of *Cicuta virosa* is of the same nature as Roman oil of chamomile (*q. v.*) (Trapp, *J. pr.* 74, 428).

CICUTENE $C_{10}H_{16}$. (160°). A dextrorotatory terpene in the essential oil obtained from the root of the water-hemlock, *Cicuta virosa* (Ankum, *Z.* 1869, 218). The same plant is said to contain an alkaloid, Cicutine (Polex, *Ar. Ph.* 18, 174; Wittstein, *Buchner's Repert.* 18, 19).

CIMICIC ACID $C_{15}H_{28}O_2$. Mol. w. 240. [44°].

Occurrence.—In the fœtid oil ejected by a kind of bug *Rhaphigaster punctipennis* when irritated. The insects are washed with alcohol, and the residue extracted with ether (Carius, *A.* 114, 147). Occurs also in spider's web (Valente, *G.* 12, 557).

Properties.—Prisms (from ether), lighter than water. Insol. water, v. sl. sol. alcohol, v. sol. ether. Has a rancid odour.

Salts.—NaA′.—KA′: amorphous.

Chloride $C_{15}H_{27}OCl$: [c. 44°].

Ethyl ether EtA′. Oil.

CIMICIC ALDEHYDE $C_{15}H_{28}O$. [72°]. Occurs in spider's web (Valente, *G* 12, 557). Reduces Fehling's solution and ammoniacal $AgNO_3$.

CINCHAMIDINE *v.* CINCHONA BASES.

CINCHENE $C_{19}H_{20}N_2$. *Cinchonidene.* [125°]. Formed by treatment of cinchonine or cinchonidine with PCl_5, and boiling the resulting cinchonine-chloride $C_{19}H_{21}Cl$ or cinchonidine chloride with alcoholic KOH. Trimetric tables *a*:*b*:*c* = ·6017:1:·5022. By heating with HCl at 220°–230° it is converted into apocinchene $C_{18}H_{17}NO$, MeCl and NH_3 being split off and H_2O taken up (Comstock a. Königs, *B.* 14, 1854; 17, 1989).

Methylo-iodide B′MeI: [186°]; monosymmetrical tables, *a*:*b*:*c* = 1·5838:1:·9114; v. sol. alcohol, sl. sol. water, scarcely sol. ether (Comstock a. Kœnigs, *B.* 18, 1219).

(α)-Cinchene-di-bromide $C_{19}H_{20}Br_2N_2$. [113°]. Formed, together with about an equal quantity of (β)-cinchene-di-bromide, by the addition of bromine to cinchene (Comstock a. Konigs, *B.* 19, 2858; 20, 2512). Monosymmetrical crystals, *a*:*b*:*c* = ·9570:1:·8686, β = 65° 52′. Converted by boiling with alcoholic KOH into dehydrocinchene. The hydrobromide forms concentric needles; the nitrate small colourless crystals, sl. sol. dilute HNO_3; the zinc-double chloride colourless needles [c. 250°].

(β)-Cinchene-di-bromide $C_{19}H_{20}N_2Br_2$ [134°]. Formed, together with (α)-cinchene-di-bromide [113°], and in about equal quantity, by the addition of bromine to cinchene. Rhombic sphenoidal hemihedral crystals, *a*:*b*:*c* = ·5552:1:1·2017. Somewhat less sol. alcohol and ether than the (α)-isomeride. Like the (α)-isomeride it is converted by boiling with alcoholic KOH into dehydrocinchene. The hydrobromide forms granular crystals more soluble than the (α)-hydrobromide (*separation*). The zinc-double chloride forms colourless needles [c. 250°]. The nitrate separates in the form of a jelly, sl. sol. dilute HNO_3 (C. a. K.).

Cinchene-bromo-hydride $C_{19}H_{21}BrN_2$. *Hydrobromcinchene.* [105°–116°]. Formed by dissolving cinchene in cooled HBr and allowing to stand for two days. Monoclinic crystals, *a*:*b*:*c* = ·8541:1:·8280, β = 63° 7′; isomorphous with cinchene-di-bromide. V. sol. alcohol, ether, benzene, chloroform, and acetic ether, sl. sol. ligroin (Comstock a. Konigs, *B.* 20, 2522).

Dehydrocinchene $C_{19}H_{18}N_2$. [c. 60° hydr.]. Obtained by boiling dehydrocinchonine chloride $C_{19}H_{19}N_2Cl$ or (α)- or (β)-cinchene-di-bromide $C_{19}H_{20}Br_2N_2$ with alcoholic KOH. Long colourless needles (with 3aq).—$B''H_2Br_2$: very soluble small prisms.—$B''H_2Cl_2PtCl_4$: very sparingly soluble red tables (Comstock a. Konigs, *B.* 19, 2857).

Apocinchene $C_{19}H_{19}NO$. [209°]. Formed by heating cinchene with HCl at 220°–230° (Comstock a. Königs, *B.* 14, 1854; 17, 1986; 18, 2379; 20, 2674). Colourless needles. Sol. alcohol, acids, and alkalis. The compounds which it forms with acids and with bases are dissociated by water.

Reactions.—By fusion with KOH or NaOH it gives oxy-apocinchene $C_{18}H_{17}NO_2$. Its ethers are oxidised by CrO_3 to cinchonic acid; on oxidation with dilute HNO_3 they yield alkyl-apocinchenic acids $C_{17}H_{13}(OR)N.CO_2H$.

Salts.—B′HBr. [c. 256°]: yellow needles (from alcoholic HBr).—B′HI.—$B'_2H_2PtCl_6$. [c. 235°]. The Ag salt is a nearly insoluble pp.

Acetyl derivative $C_{19}H_{18}AcNO$. [119°].

Methyl ether $C_{19}H_{18}(OMe)N$: oil; v. sol. alcohol, ether, &c., nearly insol. water. B′HCl ½aq: [c. 198°], crystalline solid.

Ethyl ether $C_{19}H_{18}(OEt)N$: [71°]; colourless prisms.

Bromo-apocinchene $C_{19}H_{18}BrNO$. [188°]. From apocinchene hydrobromide in chloroform and HOAc by adding Br. Crystalline, v. sol. aqueous alkalis, benzene, and chloroform, less sol. alcohol and ether. CrO_3 oxidises it to bromoform and cinchonic acid. Boiling alcoholic NaOH does not attack it.

Di-bromo-apocinchene. *Ethyl ether* $C_{19}H_{16}Br_2(OEt)N$. [118°]. From ethyl-apocinchene (10 g.) and Br (15 c.c.)

Oxy-apocinchene $C_{19}H_{19}NO_2$. [217°]. Formed by fusing apocinchene $C_{19}H_{18}(OH)N$ with KOH or NaOH (Comstock a. Kœnigs, *B.* 18, 2385). Colourless crystals. V. sol. caustic alkalis, sl. sol. cold alcohol and pure ether, nearly insol. water and dilute acids.

Acetyl derivative $C_{19}H_{18}AcNO_2$. [203°].

Methyl-apocinchenic acid $C_{17}H_{13}(OMe)N.CO_2H$. [234°]. Formed by oxidation of the methyl ether of apocinchene with dilute HNO_3 (Comstock a. Kœnigs, *B.* 18, 2383). Colourless crystals. V. sol. alcohol, acids and alkalis, nearly insol. water.

Ethyl-apocinchenic acid $C_{17}H_{14}(OEt)N.CO_2H$. Formed by oxidation of the ethyl ether of apocinchene $C_{19}H_{18}(OEt)N$ with dilute HNO_3 (Comstock a. Kœnigs, *B.* 18, 2384; 20, 2674). Crystallises from absolute alcohol in yellowish anhydrous needles [162°]; from dilute alcohol in crystals (containing aq) [126°]. By heating with HCl at 130° it is split up into CO_2, EtCl, and homo-apocinchene $C_{17}H_{15}NO\,x$aq [185°]. The hydrobromide of homoapocinchene B'HBr aq crystallises in yellow needles or prisms [222°] sl. sol. water. Homo-apocinchene on fusion with potash gives an acid [230°] split up by heat into CO_2 and another acid $C_{17}H_{11}NO_2$ (?) [223°].

Salts.—The Ag, Ca, Ba, Pb, Zn, and Cu salts are sparingly soluble. — AgA'. — $(HA')_2H_2PtCl_6$.

CINCHOL $C_{20}H_{34}O$. [139° water-free]. Is found in all true cinchona barks but not in *C. Cuprea*; in largest amount (up to 0·03 p.c.), along with some quebrachol, in *C. Calisaya Var. Ledgeriana.* Found also along with cupreol. Helms' 'Cinchocerotine' (*Ar. Ph.* [3] 21, 279) was probably wholly or partly cinchol. Further, Liebermann's 'Oxy-chino-terpene' (*B.* 17, 871) is cinchol (Hesse).

Preparation.—From crude cupreol, the acetate being separated by repeated crystallisations from alcohol from the acetates of quebrachol and cupreol (O. Hesse, *A.* 228, 288; 234, 375).

Properties. Plates (containing aq) from alcohol. Lævorotatory in chloroform solution; $[\alpha]_D = -34·3°$ (in a 6 p.c. solution). Its properties are similar to those of cupreol.

Acetyl derivative $C_{20}H_{33}O(C_2H_3O)$. [124°]. White needles from alcohol. M. sol. alcohol, v. sol. ether and chloroform. Lævorotatory (in chloroform); $[\alpha]_D = -41·7°$ (in a 4 p.c. solution).

Propionyl derivative $C_{20}H_{33}O(C_3H_5O)$. [110°]. Microscopic plates.

CINCHOCEROTIN $C_{27}H_{18}O_2$. [130°]. Probably identical with the preceding. Deposited in tubes through which an alcoholic extract of South American calisaya bark and lime is passed (Helms, *Ar. Ph.* [3] 21, 279). Chromic acid gives acetic acid, butyric acid, and cinchocerotic acid $C_{10}H_{22}O_2$ [72°].

CINCHOLEPIDINE *v.* (*Py.* 1) METHYL-QUINOLINE.

CINCHOLINE. Strongly basic oil. Volatile with steam. Occurs in the mother liquors from quinine. V. sol. alcohol and ether, less sol. water. The hydrochloride forms colourless quadratic plates. The oxalate is sparingly soluble in water (Hesse, *B.* 15, 858).

CINCHOMERONIC ACID and iso-cinchomeronic acid *v.* PYRIDINE DI-CARBOXYLIC ACID.

CINCHONA BARK. *Cortex Cinchonæ* and *Chinæ, Cortex Peruvianus, Peruvian Bark, Ecorce de Quinquina, China rinde.*—This name is given to the bark of various species of *Cinchona*, which, with about thirty other allied genera, constitute the tribe *Cinchoneæ* of the order *Rubiaceæ* (*v. Pharmacographia*, f. 338). They have been long known for their antifebrile properties, which are chiefly due to the contained alkaloids, which are absent in all the allied genera, with the exception of *Remigia*, some species of which contain them.

These medicinal barks were first introduced into Europe from Peru about the year 1638, by the Countess of Chinchon, wife of the Viceroy of Peru (in whose honour the name cinchona was given to the genus by Linnæus), and being afterwards sent over by the Jesuits, acquired great celebrity for the cure of intermittent fevers, being known by the names of Pulvis Comitessæ, Jesuiticus, Patrum, &c. The cinchonas are natives of the mountain regions of South America, on the eastern slope of the Cordillera of the Andes and on the mountain ranges of Ecuador and New Granada, growing at elevations from 3,000 to 11,000 feet, no species being known to inhabit the low alluvial plains.

In 1853 an attempt was made by the Dutch Government to introduce the cultivation of cinchona into Java, but at first great difficulty was found in obtaining seeds or plants of good qualities, owing to the extreme jealousy of the natives.

In 1860 Mr. Clements Markham was sent by the Government of India to South America to collect seeds and plants, and after great difficulties he and his coadjutors succeeded in introducing the most valuable species of cinchona into India, and Mr. C. Ledger, who was then residing on the west coast of America, also succeeded in obtaining a supply of seed of the finest variety of the Calisaya bark.

The cultivation of the cinchonas thus introduced into the East Indies has increased to such an extent that much the greater proportion of the bark is now supplied from Ceylon, Java, and India, from whence upwards of 14,000,000 lbs. of bark were imported in 1885.

This cultivation has also been successfully introduced into Jamaica and elsewhere, in tropical regions where high mountains give the requisite elevation, and in the natural home of the genus there are now large plantations of cultivated cinchonas of the finest qualities.

In collecting the bark in the native forests, the trees are invariably cut down, and the bark, when stripped off, dried either in the sun or on hurdles arranged over a fire in a hut.

In the plantations of cultivated bark, the system of cutting down the trees is adopted to some extent, but a far more economical method of harvesting the bark is by the process of 'renewing,' introduced by the late W. G. McIvor, by which a succession of crops of bark can be obtained from the same tree. For this purpose longitudinal incisions are made into the bark and about half the bark removed in alternate strips, leaving the remaining bark intact, and the stem is then covered with moss. A fresh layer of bark is then formed from the cambium with surprising rapidity, and in a few months it attains the thickness of the original bark when several years old.

It is remarkable that the renewed bark is not only in most cases richer in total alkaloids than the natural bark but contains a far higher proportion of quinine, which appears to take the place of the less valuable alkaloids. Another more imperfect process adopted for renewing barks is to cut off the external layers with a spoke shave, but the results are rarely so good as in the former process, as it is essential that the liber layers of the bark should be cut through without injuring the cambium beneath, which is more difficult to do in this manner than in the other system.

Between thirty and forty species of cinchona have been described, but most of them are of no practical value. Those used in pharmacy and in the manufacture of quinine are as follows.

I. *Yellow or Calisaya Bark.* This is the most valuable of all the species of cinchona. It is found in commerce in quills formed by the contraction of the bark when drying, which are covered with a rough epidermis. It was formerly found also in flattened pieces, from which the epidermis had been removed, and which have been dried under pressure, and was then known as flat yellow bark.

II. *Crown bark. Pale bark. Loxa bark* yielded by *C. officinalis* and the allied species, found in quills, with a rough blackish-brown or dark grey surface. This was formerly the chief bark used in medicine under the name of Peruvian bark. It is largely cultivated and approaches the Calisaya in richness.

III. *Red bark, Cinchona Rubra and Succirubra,* so called from the red colour of the sap and of the mature bark. Owing to the vigorous growth of this species, it has been cultivated in India to a very large extent, and has been adopted in the British Pharmacopœia for use in galenical preparation. It is less suited for the preparation of quinine, owing to the great proportion of cinchonidine that it contains.

IV. *Soft bark. Columbian and Carthagena bark,* yielded by *C. Lucumifolia and Lancifolia,* imported in quills or broken pieces, with a whitish shining epidermis, which scales off easily. They vary greatly in the quantity and quality of the alkaloids.

V. *Pitayo barks,* yielded by *C. Pitayensis,* are imported in short curly pieces of a brownish colour, either bare or with a rugged whitish epidermis. They are rich in alkaloids, especially quinine and quinidine.

VI. *Cuprea bark,* yielded by *Remigia Pedunculata.* Although not a true cinchona bark, this may conveniently be included here as the only known species of any other genus that has yielded the cinchona alkaloids. It is imported in short quills and broken pieces of a deep red colour. The bark is of a very compact texture, of much higher specific gravity than the true cinchonas. It gives with ammonia a purple solution of considerable tinctorial power. It contains quinine, quinidine, cinchonine, but no cinchonidine, and an alkaloid, cupreine, discovered by Paul and Cownley, which exists in the bark in a combination with quinine, previously taken for a distinct alkaloid, and designated homoquinine, an allied species. *R. Purdicana* yields no quinine, but a new alkaloid called by the discoverer, M. Arnaud, Cinchonamine.

Along with these principal species are found in commerce the bark of a great number of species of *Cinchona,* most of which contain little or no valuable alkaloid, and also barks of allied genera, especially of *Ladenbergia* and *Exostemma.* These barks contain none of the cinchona alkaloids.

The organic constituents of cinchona bark are quinine, quinidine, cinchonine and cinchonidine, and some isomeric modifications of these bases, quinamine, uncrystallisable alkaloids, in some species aricine, paricine, and their congeners; quinic acid, quinovin and cinchotannic acid, cinchona red, colouring matter, wax, and fatty matter, a small quantity of volatile oil, along with starch, gum, and woody fibre.

The barks of some of the allied genera also contain quinovin, cinchotannic acid, and quinic acid. The ash of cinchona bark consists chiefly of calcic and potassic carbonate, containing also, besides iron, a notable quantity of manganese. For detailed analysis vide Carles, *Ph.* [3] 3, 723.

The first chemical examination of cinchona bark appears to have been made in 1785 by Hermbstädt, who obtained from it calcium quinate, which he designated as essential salt of quinine. Schneider in 1807, and Vauquelin in 1808, separated quinic acid from the calcium salt. Quinotannic acid was discovered by Deyeux in 1793, and obtained in a more definite form by Séguin in 1797. Cinchona bitter and cinchona red were obtained from red cinchona bark by Reuss in 1810. The first discovery of the alkaloids was made by Gomes of Lisbon in 1811, who appears to have obtained cinchonine in an impure state; but its true nature was not discovered till 1820, when Houton-Labillardière drew attention to its alkaline reaction, and communicated his observations to Pelletier and Caventou, who in the same year succeeded in isolating first cinchonine, and afterwards quinine, and proved them to be true vegetable alkaloids. The isomeric modifications of these alkaloids were afterwards discovered and variously named. Pasteur (*C. R.* 36, 26; 37, 110) reduced those then known to four, quinine and its isomeride, quinidine, and cinchonine and its isomeride, cinchonidine, and also investigated the isomeric modifications of these alkaloids produced by the action of heat in strong acid solution, viz. quinicine and cinchonicine. Hesse has now investigated the whole subject, and has described various alkaloids which, however, with the exception of a modification of cinchonidine named by him 'homo-cinchonidine,' and the recently discovered hydroquinine, do not seem to have been isolated by other observers.

Cinchona barks are employed medicinally in the form of tinctures, fluid extracts, and infusions, and were thus used long before the discovery of the alkaloids, and, although it is to these bodies that the medicinal value is chiefly due, the cinchotannic acid and other ingredients appear also to be of medicinal value.

Reactions of Cinchona bark.—Most salts of the cinchona alkaloids give a purple tar when strongly heated in a test-tube, especially if they are mixed with cellulose. The same reaction is observed when a bark containing them is heated, and is very characteristic. The test was proposed by Grahe, of Kasau, in 1858. Water extracts a portion only of the alkaloidal contents of cinchona bark, and the cinchotannates of the alkaloids being more soluble in hot than in cold water, a hot infusion becomes turbid on cooling. The solution obtained by treatment with acidulated water gives the following reactions:—The alkaloids give a whitish precipitate with excess of caustic alkali, and with tannic acid, and a yellow crystalline precipitate with platinic chloride, if these precipitates are submitted to dry distillation, the characteristic odour of quinoline is observed. Of the acid constituents quinotannic acid gives precipitates white with solution of gelatin, green with ferric salts, dirty white with tartar emetic. Quinovic acid gives, with sulphate of copper, first a green colour and then a precipitate which, when washed, has a bitter metallic taste. Quinic acid distilled with sulphuric acid and manganese peroxide yields a distillate of quinone; this test is proposed by Stenhouse (*Mem. Chem. Soc.* ii. 226) to distinguish true cinchona bark.

For the **quantitative analysis** of cinchona bark, various processes have been proposed, many of which give good results in practised hands, but in all of which success largely depends on details of manipulation only to be acquired by practice. The earlier processes depended on dissolving out the alkaloids with hydrochloric acid, precipitating the alkaloids by caustic alkali. A great excess of acid is required for the extraction of the whole alkaloid, and a great excess of alkali for the complete separation of the alkaloids from the cinchotannic acid which precipitates along with them by exact neutralisation. Better methods are those in which the salts of the alkaloids are decomposed in the bark by treatment with alkali, and the alkaloids then extracted by suitable solvents. De Vrij (*Pharmacographia*, p. 365, and *Ph.* [3] 4, 241) recommends to mix 20 g. of powdered bark with milk of lime (5 g. lime to 50 c.c. water), dry the mixture slowly, stirring frequently. Then boil the dry powder with 200 c.c. alcohol of S.G. 0·830, pour off and filter the solution, and boil again with 100 c.c. alcohol, throw the whole on the filter, and wash further with 100 c.c. alcohol, acidulate with dilute sulphuric acid, filter, and distil, but not to dryness (water must be added if necessary), when all the spirit is separated the aqueous solution is filtered. The filtrate and washings are reduced to 50 c.c., and while still warm treated with caustic soda in excess. After cooling, the solution is decanted off and water added before throwing it on the filter. It is then washed with the smallest possible quantity of water, pressed between folds of blotting paper, dried, and weighed. The weight is that of the total alkaloids in the bark.

The process given in the *British Pharmacopœia*, f. 111, is also a good one, it is as follows:—Mix 200 grams of the bark in fine powder with 60 grams of hydrate of calcium; moisten the powders with half an ounce of water, mix the whole intimately; allow it to stand for an hour or two, it will then present the characters of a moist dark-brown powder, in which there should be no lumps or visible white particles. Transfer the powder to a flask, boil for half an hour with three fluid ounces of a mixture of three volumes of benzene and one of amylic alcohol, decant and filter the solution, leaving the bark in the flask, boil again with the same solvent and decant as before; repeat the third time, and finally throw the bark on the filter and wash with the solvent. The filtrates are then shaken repeatedly with water acidulated with hydrochloric acid till the alkaloids are all removed, the acid washings concentrated, and if the process given below for the separation of the alkaloids is adopted, the alkaloids are precipitated by excess of alkali.

The process given in the German *Pharmacopœia* is also efficient.

The **separation of the cinchona alkaloids** depends on their relative solubilities in various reagents, but in most cases these do not differ so widely as to give a perfectly satisfactory separation, and the separation is made more difficult by the tendency of the alkaloids and their salts to form more or less definite compounds with one another.

A convenient process giving fairly accurate results is as follows:—Treat the powdered mass of mixed alkaloids with ten times its weight of ether; this will dissolve the quinine and amorphous alkaloid, and small quantities only of the other alkaloids; wash the alkaloids out of this ethereal solution by excess of dilute sulphuric acid, and neutralise after heating to boiling with dilute ammonia, using no more water than is necessary; the quinine will then, on cooling, crystallise out almost entirely as sulphate, which salt is almost insoluble in a cold solution containing ammonic sulphate. The crystals after filtration and washing with a small quantity of water are pressed between blotting paper and dried at 100°. 73·4 pts. of the anhydrous salt equal 100 of the hydrated crystals. The salt should be tested for cinchonidine, which may be present in small quantity. The alkaloids contained in the mother liquor are then precipitated by alkalis, converted into neutral acetates, and a solution of potassium iodide and a small quantity of alcohol is then added; on standing quinidine iodide will crystallise out if present. Of this salt 100 pts. equal 71·8 of the alkaloid. A solution of potassio-tartrate of sodium is then added to the mother liquor, and on agitation and standing, tartrate of cinchonidine will crystallise out if any of that alkaloid has been dissolved by the ether; 100 pts. of this salt equal 80·4 of the alkaloid. The mother liquor now contains amorphous alkali, which may be precipitated by a solution of sodic hydrate and weighed. The portion insoluble in ether must be also converted into neutral acetates, and the solution tested for quinidine by potassic iodide, a few drops of spirit being added, and for cinchonidine by potassio-tartrate of sodium as above. If a considerable proportion of this alkaloid is present it will probably contain a notable quantity of quinine, as ether fails to give a complete separation. After removal of any quinidine and cinchonidine present by those reagents, the solution contains the cinchonine, which may be precipitated by caustic alkali and weighed. Dr. de Vrij recommends that the quinine should be precipitated from the solution of alkaloids soluble in ether, as iodosulphate (*Ph.* [3] 6, 461); in skilful hands this method of analysis gives accurate results. Instead of commencing the separation of the alkaloids by ether, Dr. Moens recommends that the neutral aqueous solution of the mixed alkaloids be treated with excess of solution of sodic potassio-tartrate, which throws down the whole of the quinine and cinchonidine as tartrates. The tartrate is then decomposed by alkali, and the quinine and cinchonidine separated by ether, the alkaloid dissolved in the ether being either weighed directly as quinine or preferably converted into sulphate and weighed as such. Great care must be taken in this case to decompose the tartrate entirely, to avoid underestimating the quinine.

The method of estimating the relative proportions of quinine and cinchonidine in the precipitated tartrates by determination of the specific rotation of the polarised ray has been recommended by Drs. De Vrij and Oudemans, but no published process for bark analysis gives the tartrate obtained direct from the crude mixed alkaloids in a sufficient state of purity to give really trustworthy results by this method.

The **distribution of the alkaloids in the bark** has been the subject of careful observation. It was first observed by Carles (*Ph.* [3] 3, 643) that though quinine exists in all portions of the bark, it is contained in much larger proportion in the external and cortical layers than in the internal liber layers, and his observation has been confirmed by other observers.

On the other hand, the corky epidermis found in some barks, specially in certain varieties of officinalis, such as the knotty bark of Jussieu does not contain alkaloid.

Alkaloids begin to form in the bark even when very young, and increase in quantity until the bark is mature, the maximum yield being attained at ages varying with the species and circumstances of growth—from five to fifteen years, or even later. The relative proportion of the different alkaloids also varies greatly in the same tree.

The increase of the dextrogyrate alkaloids, quinidine and cinchonine, in the root barks is remarkable. This is specially the case in stunted or unhealthy trees in which the root bark is often exceptionally rich in alkaloid. As a rule a luxuriant growth of the plant is required to give the maximum of alkaloid, and therefore it is natural that manures should have a beneficial effect. Valuable experiments on this subject have been carried out by Mr. Broughton at the Government Plantation at Ootacamund (*Ph.* [3] 8, 521). He found that a great improvement in the yield of quinine was caused by the use of guano, a greater by the use of ammonia salts, but most of all by the use of farmyard manure. A series of experiments on renewed bark of *C. succirubra* in Ceylon, on the other hand, showed a maximum of improvement from the use of bones; ammonia and cattle manure producing less improvement, the different result being, no doubt, owing to a different condition of the soil. In some soils a very great improvement is caused by dressings of lime. This question is one deserving of much more investigation than it has yet received. D. H.

CINCHONA BASES.—Quinine, Cinchonine, Cinchonidine, and Aricine are described in separate articles. The existence of many of the following bases requires confirmation. In the names of these alkaloids *qu* is used before *i*, and *ch* before any other vowel.

Chairamine $C_{22}H_{26}N_2O_4$ aq. [140°]. [233° when dry] $[\alpha]_D$ = about +100°. In the bark of *Remijia Purdieana* (Hesse, *A.* 225, 243). Named from χαίρω, because Hesse 'rejoiced' at discovering it. Slender needles (containing aq) (from dilute alcohol). Sol. ether and chloroform. Its alcoholic solution is alkaline to litmus. H_2SO_4, with or without MoO_3, forms a colourless solution, turning dark green.

Salts.—B′HCl aq. Needles. - $B'_2H_2SO_4$ 8aq. - $(B'HCl)_2PtCl_4$ 2aq.

Conchairamine $C_{22}H_{26}N_2O_4$aqEtOH. [82°-86°]; B′aq [c. 110°]; B′ [c. 120°] $[\alpha]_D$ (for B′) = +68·1 in 2 p.c. alcoholic solution. In the bark of *Remijia Purdieana* (Hesse, *A.* 225, 216). It has three melting-points according as it is dry, with water of crystallisation, or with alcohol of crystallisation also. Colourless prisms (containing aqEtOH) (from alcohol). Sol. ether and chloroform. Conc. H_2SO_4, with or without MoO_3, forms a brown solution turning green.

Salts. — B′HCl. — $(B'HCl)_2PtCl_4$ 5aq. — B′HI aq.—B′HSNC aq.—$B'_2H_2SO_4$ 9aq.

Methylo-iodide.—B′MeI aq. Red crystals. B′MeI 3aq. Colourless crystals.

Methylo-chloride. -B′MeCl 2aq. Platino-chloride.—$(B'MeCl)_3HCl(PtCl_4)_2$ 14aq.

Chairamidine $C_{22}H_{26}N_2O_4$ aq. [c. 128° when dry]. $[\alpha]_D$ = +7·3° in 3 p.c. alcoholic solution. In the bark of *Remijia Purdieana* (Hesse, *A.* 225, 253). Amorphous powder, insol. water, sol. ether, alcohol, benzene, and chloroform; solution in conc. H_2SO_4 slowly turns green. Animal charcoal removes it from solution in acetic acid.

Salts.—$(B'HCl)_2PtCl_4$ 5aq. -Sulphate is gelatinous.

Conchairamidine $C_{20}H_{26}N_2O_4$ aq. [115° when dry]. $[\alpha]_D$ = −60° in a 3 p.c. alcoholic solution. In the bark of *Remijia Purdieana* (O. Hesse, *A.* 225, 256). Crystalline. V. sol. ether, alcohol, chloroform, benzene, and acetone. Its alcoholic solution is neutral to litmus. In conc. H_2SO_4, with or without MoO_3, the solution is dark green.

Salts. — Well crystallised. — B′HCl 3aq. — $(B'HCl)_2PtCl_4$ 5aq.—$B'_2H_2SO_4$ 14aq.

Cinchamidine $C_{20}H_{26}N_2O$. [230°]. $[\alpha]^D$ = −98·4. Occurs in the mother-liquors from homocinchonidine (Hesse, *B.* 14, 1683; *cf.* Forst a. Bohringer, *B.* 14, 1270; 15, 520). Colourless plates, needles, or prisms. Sol. alcohol and chloroform, sl. sol. ether, insol. water. Has an alkaline reaction.

Salts. — B′HCl 2aq: trimetric prisms. — $(B'HCl)_2PtCl_4$ 3aq: yellow amorphous pp. — $B'H_2Cl_2PtCl_4$: orange plates. — Tartrate $B'_2C_4H_6O_6$ 2aq: colourless prisms, sl. sol. cold water.

Cinchonamine $C_{19}H_{24}N_2O$. [194°] (A.); [185°] (H.). $[\alpha]_D$ = +121° (1 pt. base in 50 pts. of 97 p.c. alcohol at 15°).

Occurrence.*—In *Cinchona Purdieana (Arnaud, *C. R.* 93, 593; 97, 174; Hesse, *A.* 225, 218; Planchon, *J. Ph.* [5] 5, 352).

Properties.—Colourless hexagonal prisms (Friedel, *C. R.* 105, 985). Sol. alcohol, ether, chloroform, CS_2 and benzene; sl. sol. petroleum or water. Highly poisonous. Its alcoholic solution is alkaline and gives no colour with Fe_2Cl_6 or Cl and NH_3. In conc. H_2SO_4 forms reddish-yellow solution, in conc. HNO_3 a bright yellow solution. In HCl it is insoluble, and on heating at 150° it gives no MeCl.

Salts.—B'HCl.—B'HCl aq.—$(B'HCl)_2PtCl_4$.—B'HBr.—B'HI.—B'HSCN.—$B'HNO_3$. S. ·2 at 15°.—$B'_2H_2SO_4$. $[\alpha]_D = +36·7°$ at 15° in 2 p.c. solution (H.); $= +43·5$ at 15° (A.). V. sol. water. $B'H_2SO_4$ $[\alpha]_D = 34·6°$. — $B'H_2S_2O_6$. — Tartrate $B'_2H_6C_4O_6$. S. 1·15 at 15°.—Malate $B'C_4H_6O_5$aq: S. 1 at 15°.—Citrate: prisms. S. 1·95 at 16°.

Acetyl derivative $C_{19}H_{23}AcN_2O$. [80°–90°]. Amorphous. Sol. acetic acid, ether, alcohol, and chloroform, sparingly so in dilute HCl. In conc. H_2SO_4 it forms a purple solution, turned yellow by heat. Not saponified by alcoholic potash.

Di-nitro-cinchonamine $C_{19}H_{22}(NO_2)_2N_2O$. [118°]. Formed by treatment with HNO_3 of S.G. 1·06. Explosive. Flocculent pp., sol. acetic acid, ether, chloroform, and alcohol, and in dilute HCl.—$(C_{19}H_{22}(NO_2)_2N_2OHCl)_2PtCl_4$.

Methylo-iodide B'MeIaq.

Methylochloride B'MeCl.—$(B'MeCl)_2PtCl_4$. The hydrate B'MeOH gives methyl-cinchonamine on boiling with water.

Methyl-cinchonamine $C_{19}H_{23}MeN_2O$. [139°]. Amorphous powder, v. sol. alcohol, ether, and chloroform, insol. water. Sulphomolybdic acid is slowly turned dark blue by it. Forms a flocculent platino-chloride $(C_{19}H_{23}MeN_2OHCl)_2PtCl_4$ 4aq.

Ethylo-iodide B'EtI. Insol. water. When treated with AgCl and $PtCl_4$ successively it gives $(B'EtCl)_2PtCl_4$ 2aq. And with Ag_2SO_4 it gives $(B'Et)_2SO_4$. When an alcoholic solution of B'EtI is boiled with addition of a little NaOH, ethyl-cinchonamine is formed.

Ethyl-cinchonamine $C_{19}H_{23}EtN_2O$,aq. [75°–78°]; when dry it melts at [c. 140°]. Amorphous, resembling methyl-cinchonamine. Platino-chloride: $(C_{19}H_{23}EtN_2OHCl)_2PtCl_4$ 3aq.

Cincholine. An oily alkaloid which accompanies quinine (Hesse, *B.* 15, 858).

Hydrocinchonidine $C_{19}H_{24}N_2O$. [229°–230°] $[\alpha]_D = 98·4$ (in 97 p.c. alcohol, $p = 2$) (Forst a. Bohringer, *B.* 14, 1270; 15, 520; O. Hesse, *B.* 14, 1893; *A.* 214, 1). Found in the mother-liquors from which cinchonidine sulphate or homo-cinchonidine sulphate has crystallised. Six-sided plates (from hot dilute alcohol) or short prisms (from strong alcohol). Less sol. alcohol than cinchonidine or homo-cinchonidine. V. sl. sol. chloroform, ether, or water. Freshly ppd. sl. sol. ether, quickly separating again in six-sided plates. Alcoholic solution is alkaline and bitter.

Reactions.—1. Its sulphate does not at once bleach $KMnO_4$ and shows no fluorescence.—2. *Ammonia* gives, in solutions of its salts, a flocculent pp. becoming crystalline; in very dilute solutions a crystalline pp. after some time.—3. *Chlorine* and NH_3 give no colour.—4. Conc. H_2SO_4 dissolves it without colour.—5. Insoluble in KOH, baryta or lime.—6. HCl (S.G. 1·125) at 160° has no action.

Salts.—(Hesse.) B'HCl 2aq.—B'CNSH.—$B'_2H_2PtCl_6$ 3aq.—$B'H_2PtCl_6$.—$B'C_7H_{12}O_6$ (quinate).—$B'_2H_2C_2O_4$.—$B'_2C_4H_6O_6$ (tartrate).—$B'_2H_2S_2O_6$ aq.—$B'H_2SO_4$ 4aq.—$B'_2H_2SO_4$ 7aq. S 1·75 at 10°. $[\alpha]_D = -75·2°$ (in water, $p = 2$); $-93·8°$ (in 97 p.c. alcohol).—$B'_2C_6H_4(OH)SO_3H$ 5aq.

Acetyl derivative $C_{19}H_{21}AcN_2O$. [42°]. $[\alpha]_D = -29·5°$ (in 97 p.c. alcohol, $p = 2$); $-50·9°$ (in water with 3HCl, $p = 2$). Amorphous hygroscopic mass. V. sol. alcohol. Saponified by alcoholic KOH. Soluble in acids forming salts, *e.g.* $C_{19}H_{23}AcN_2OH_2PtCl_6$ 2aq.

Amorphous hydrocinchonidine $[\alpha]_D = -12°$ (in water with 3HCl, $p = 2$). Is formed by fusing the sulphate at 140°, and adding aqueous NaOH to the product. It is a brownish amorphous base, isomeric with hydrocinchonidine. It is v. sol. ether, alcohol, chloroform, or acids. Its salts are amorphous, *e.g.* $B'H_2PtCl_6$ 2aq.

Di-cinchonine $C_{38}H_{44}N_4O_2$. [40°]. $[\alpha]_D = +66°$. Occurs in the bark of *Cinchona rosulenta* and of *C. succirubra* especially. Not present in the bark of *C. Calisaya, var. Boliviana*, and *var. Ledgeriana, C. Tucujensis* or *C. Pelletierana*, or of *Remijia pedunculata* or *R. Purdieana* (O. Hesse, *A.* 227, 153).

Properties.—Yellowish amorphous base. V. sol. ether, acetone, alcohol, chloroform, and benzene, less sol. water and light petroleum, insol. in aqueous NaOH. Its alcoholic solution is strongly alkaline and tastes bitter, gives no colour with Cl and NH_3, and is dextrorotatory.

Salts.—The base dissolves in dilute acids and is reppd. by NH_3 or NaOH as a resinous pp.—B″2HCl.—B″2HCl.$PtCl_4$.

Reaction.—HCl at 150° converts it into di-apocinchonine, which is also formed from cinchonine under similar conditions.

Hydrocinchonine $C_{18}H_{24}N_2O$. [256°]. Occurs in *C. cuprea* (Hesse, *B.* 15, 855).—$B''H_2PtCl_6$ 2aq.

Cinchotine $C_{19}H_{24}N_2O$. [277° cor.]. S. ·07 at 20°; S. (ether) ·19 at 20°. Occurs in crude cinchonine sulphate (Willm a. Caventou, *A. Suppl.* 7, 248; Forst a. Bohringer, *B.* 14, 436; 1267; 15, 519; Skraup, *A.* 197, 352; *C. C.* 1877, 629). Slender prisms and scales. Dextrorotatory. On oxidation it gives cinchonic acid.

Salts.—$B'_2H_2SO_4$ 12aq: fine needles or prisms. S. 3·28 at 13°.—$B'HNO_3$ aq: tables.—B'HCl 2aq: fine needles.—$B'H_2Cl_2$.—B'HCl 2aq: S. 2·12 at 0°.—B'HBr 2aq.—$B'H_2Br_2$: prisms.—B'HI aq.—Sulphocyanide B'CNSH: long needles, sl. sol. water.—Oxalate $B'_2H_2C_2O_4$ aq: needles; S. 1·16 at 10°.—Tartrates $B'C_4H_6O_6$ 4aq: needles, sol. hot water.—$B'_2C_4H_6O_6$ 2aq: prisms.—Benzoate $B'C_7H_6O_2$: needles, sl. sol. cold water.

Quinamine $C_{19}H_{24}N_2O_2$. [172°]. $[\alpha]_D = 93·5°$ (in a 2 p.c. chloroform solution), $[\alpha]_D = 104·5°$ (in a 2 p.c. alcoholic solution). S. ·064 at 16°. S. (ether) 2 at 16°. Occurs in the bark of *Cinchona succirubra*, and of many other species of cinchona (Hesse, *A.* 166, 266; 182, 163; 199, 335; 207, 288; De Vrij, *Ph.* [3] 4, 609; *J.* 1874, 874). Obtained from the mother-liquor after quinine and cinchonine have been ppd. as tartrates. Long prisms (from dilute alcohol). Dextrorotatory. Its alcoholic solution is alkaline to litmus. $AuCl_3$ gives a yellowish pp. which soon turns purple. Paper moistened with an acid solution of the sulphate is turned green, and finally blue, by Cl_2O_4.

Salts.—$B'HCl$ aq: prisms.—$B'H_2PtCl_6$ 2aq.—$B'HClO_3$.—$B'HBr$ aq.—$B'HI$. S. 1·4 at 16°.—$B'HNO_3$.

Quinamidine $C_{19}H_{24}N_2O_2$. [93°]. $[\alpha]_D$ = 4·5° (in a 2 p.c. alcoholic solution). Formed by the action of acids upon quinamine (Hesse, *A.* 207, 299). Nodules; v. e. sol. alcohol. Not ppd. by NH_3 from acid solutions, but ppd. by NaOH. $AuCl_3$ gives a purple colour in solutions of its hydrochloride.—$B'HCl$ aq.—$B'_2H_2PtCl_6$ 6aq.—$B'HBr$ aq.—**Oxalate** $B'_2H_2C_2O_4$ 4aq.

Quinamicine $C_{19}H_{24}N_2O_2$. [109°]. $[\alpha]_D$ = 3·8° (in a 2 p.c. alcoholic solution). Formed by heating quinamine with dilute acids at 130° (Hesse, *A.* 207, 303). Amorphous, but gradually becomes crystalline. V. e. sol. alcohol. Dextrorotatory.—$B'_2H_2PtCl_6$ 3aq.

Protoquinamicine $C_{17}H_{20}N_2O_2$. Formed by heating dry quinamine acid sulphate at 130° (Hesse, *A.* 207, 305). Amorphous brown base.—$B'_2H_2PtCl_6$.

Apoquinamine $C_{19}H_{22}N_2O$. [114°]. Formed by boiling quinamine with excess of HCl (S.G. 1·125) for 3 minutes (Hesse, *A.* 207, 294). The alcoholic solution is inactive and neutral to litmus: the hydrochloride is lævorotatory.—$B'HCl$ ½aq.—$B'_2H_2PtCl_6$ 2aq.—$B'HNO_3$. **Oxalate** $B'_2H_2C_2O_4$ aq. **Tartrate** $B'_2C_4H_6O_6$ *x*aq.

Acetyl derivative $C_{19}H_{21}AcN_2O$. Amorphous.—$B'_2H_2PtCl_6$ 2aq.

Conquinamine $C_{19}H_{24}N_2O_2$. [123°]. $[\alpha]_D$ - 205° (in a 2 p.c. alcoholic solution). S. (91 p.c. alcohol) 13·5 at 19°; S. (ether) 13·5 at 15°; S. (benzene) 24·4 at 18°; S. (CS_2) 6·05 at 18°. Occurs in the bark of *C. succirubra* and *rosulenta.* It is best separated from quinamine through the greater solubility of its salts (Oudemans, *A.* 209, 38; Hesse, *A.* 209, 62).

Properties.—Long prisms or pyramids. It resembles quinamine in its reactions with H_2SO_4 and HNO_3. Gold chloride gives a golden pp. followed by a purple colouration. Heating with HCl forms apoquinamine $C_{19}H_{22}N_2$.

Salts. $B'HCl$: octahedra, m. sol. water; $[\alpha]_D$ = 205°.—$B'H_2PtCl_6$ 3aq (O.).—$B'H_2PtCl_6$ aq (H.).—$B'HClO_3$.—$B'HClO_4$.—$B'HBr$.—$B'HI$. S. 9·4 at 16°.—$B'HNO_3$.—$B'_2H_2SO_4$.—**Formate** $B'CH_2O_2$: monoclinic crystals. — **Acetate** $B'HOAc$: dimetric crystals. — **Oxalate** $B'_2H_2C_2O_4$ 3aq. — **Quinate** $B'C_7H_{12}O_6$ 2aq: prisms.

Quinidine $C_{20}H_{24}N_2O_2$. *Conquinine.* [168°]. $[\alpha]_D$ = 236·8 − 3*p* (in a *p* p.c. alcoholic solution). S. ·05 at 15°; S. (ether) 3 at 10°. Occurs in the bark of *Cinchona Calisaya*, *C. pitayensis*, and other species of *Cinchona* (van Heijningen, *A.* 72, 302; Pasteur, *C. R.* 36, 26; Stenhouse, *A.* 129, 15; Hesse, *A.* 146, 357; 166, 232; 174, 338; 176, 225; 182, 163; *B.* 10, 2154; 12, 425; Oudemans, *A.* 182, 53). By adding NaOH to the mother-liquors from which quinine sulphate has separated crude quinidine is ppd. Pure quinidine may be isolated from this by means of its iodide. Prisms (containing 2½aq) (from alcohol), rhombohedra (containing 2aq) (from ether), or laminæ (containing 1½aq) (from water). Its solution in dilute H_2SO_4 fluoresces blue. Chlorine-water and NH_3 give a green colour. Dilute H_2SO_4 at 100° changes it to quinicine. Conc. HCl converts it on heating into apoquinidine and apoquinidine chlorohydride. It is a febrifuge. It crystallises in trimetric forms with various alcohols: $B'MeOH$; $B'EtOH$; $B'PrOH$; $B'C_3H_5OH$; and $B'_2C_2H_4(OH)_2$ (Mylius, *B.* 19, 1773).

Salts.—$B'HCl$ aq. S. 1·6 at 10°; $[\alpha]_D$ = 212 − 2·56 *p* (in a *p* p.c. alcoholic solution).—$B'H_2Cl_2$ aq: $[\alpha]_D$ = 250° in a 2 p.c. aqueous solution.—$B'H_2ZnCl_4$.—$B'_2H_2ZnCl_4$.—$B'_2H_2HgCl_4$.—$B'H_2PtCl_6$ aq.—$B'_2H_2PtCl_6$ 3aq.—$B'H_2AuCl_4$.—$B'HBr$. S. ·5 at 14° (de Vrij, *J. Ph.* [3] 32, 328).—$B'HI$. S. ·08 at 15°.—$B'H_2I_2$ 3aq. S. 1·1 at 15°.—$B'HNO_3$. S. 1·2 at 15°.—$B'AgNO_3$.—$B'_2H_2SO_4$ 2aq. S. 1 at 15°. $[\alpha]_D$ = 184° in a 3 p.c. solution in chloroform.—$B'H_2SO_4$ 4aq. S. 11·5 at 10°.—$B'_2H_2SO_4H_2I_6$ (Jorgensen, *J. pr.* [2] 14, 356; 15, 67).—$B'_4(H_2SO_4)_3H_2I_{10}$. $B'_2H_2SeO_4H_2I_6$.—$B'_4(H_2SeO_4)_3H_3I_{11}$.—$B'_2H_2S_2O_3$ 2aq.—$B'H_3PO_4$.—$B'_2H_2CrO_4$ 6aq: large yellow plates (Hesse, *A.* 213, 144).—**Oxalate** $B'_2H_2C_2O_4$ aq. S. ·66 at 15°.—**Succinate** $B'_2C_4H_6O_4$ 2aq.—**Tartrate** $B'_2C_4H_6O_6$ aq. S. 2·6 at 15°.—**Acid tartrate** $B'C_4H_6O_6$ 3aq. S. ·25 at 10°.—$B'C_4H_4(SbO)O_6$ 4aq. S. ·18 at 10°.

Acetyl derivative $C_{20}H_{23}AcN_2O_2$. $[\alpha]_D$ = 128° in a 2 p.c. alcoholic solution at 15°. Amorphous.—$B'H_2PtCl_6$ 3aq.—$B'H_2Au_2Cl_8$ 2aq.

Methylo-iodide $C_{20}H_{24}N_2O_2MeI$: needles (Stahlschmidt, *A.* 90, 221).—$B'MeI_3$ [165°] (Jorgensen, *J. pr.* [2] 3, 153).

Ethylo-iodide $C_{20}H_{24}N_2O_2EtI$ (Stenhouse, *A.* 129, 20).—$B'EtI$ aq (Howard, *C. J.* 26, 1183).—$B'EtCl$ aq.—$B'EtHPtCl_6$.—$B'_2Et_2I_6H_2SO_4$.

Quinidine chloride $C_{20}H_{23}N_2OCl$. *Conquinine chloride.* [132°]. Formed by the action of PCl_5 upon the hydrochloride of quinidine (conquinine) (Comstock a. Konigs, *B.* 18, 1223). Colourless crystals. V. sol. alcohol, benzene, and chloroform, sl. sol. ligroin and dry ether. By boiling with alcoholic KOH it is converted into quiniene $C_{20}H_{22}N_2O$.

Apoquinidine $C_{19}H_{22}N_2O_2$. *Apoconquinine.* [137°]. $[\alpha]_D$ = 155° (in a 2 p.c. alcoholic solution). Formed, together with MeCl, by heating quinidine with conc. HCl. White, amorphous powder (containing 2aq). Sol. alcohol and ether, $[\alpha]_D$ = 153·3 *p* = 2, *t* = 15° in 97 p.c. alcohol. The solution in dilute H_2SO_4 does not fluoresce, and gives no green colour with Cl and NH_3 (Hesse, *A.* 205, 326).

Hydrochloride: acicular crystals, v. sol. water.—$B'H_2PtCl_6$ 3aq: yellow flocculent pp.

Diacetyl derivative $C_{19}H_{20}Ac_2N_2O_2$. $[\alpha]_D$ = 40·4° in a 2 p.c. solution in 97 p.c. alcohol at 15°. Its sulphate fluoresces blue, and gives a green colour with Cl and NH_3.—$B'H_2PtCl_6$ 2aq: golden crystalline pp.

Apoquinidine chlorohydride $C_{19}H_{23}ClN_2O_2$. Formed by heating quinidine or apoquinidine with fuming HCl at 150°. Crystalline (with 2aq) or amorphous when anhydrous [164°]. Sol. ether and alcohol. $[\alpha]_D$ = 203·7° (*p* = 2, *t* = 15·97 v.p.c. alcohol). Does not give a green colour with Cl and NH_3.—$B'2HCl$.—$B'H_2PtCl_6$ 4aq.

Diacetyl derivative $C_{19}H_{21}Ac_2ClN_2O_2$. [168°]. Gives no green colour with Cl and NH_3. $[\alpha]_D$ = 95° in a 2 p.c. solution in dilute HCl.—$B'H_2PtCl_6$ 3aq.

Iso-quinidine $C_{20}H_{24}N_2O_2$. Formed by dissolving quinidine in conc. H_2SO_4 (Hesse, *A.* 243, 149). Long needles (from ether).— $B'_2H_2SO_4$ 8aq: needles.—$B'H_2PtCl_6$ 3aq: yellow flocculent pp.

Quiniène $C_{20}H_{22}N_2O$. *Quinene.* [81°]. Formed by treatment of quinine or quinidine with PCl_5 followed by alcoholic KOH (Comstock a. Königs, *B.* 17, 1989; 18, 1223). Trimetric crystals (containing 2aq), *a:b:c* = ·5322:1: ·6642. The solution in dilute H_2SO_4 shows a greenish-blue fluorescence. By heating with HBr (or HCl) it is converted into apoquiniène $C_{18}H_{17}NO_2$.

Salts.—$B''H_2Cl_2ZnCl_2$ 2aq: trimetric prisms, *a:b:c* ·3124:1: ·4964. The **tartrate** is sl. sol. cold water, and well crystallised.

Dibromide $C_{20}H_{22}Br_2N_2O$. Obtained by addition of bromine to quiniène. By boiling with alcoholic KOH it is converted into dehydroquiniene $C_{20}H_{20}N_2O$. The *hydrobromide* $B''H_2Br_2$ 2aq forms yellow crystals, sl. sol. alcohol, aqueous HBr, or cold water (Comstock a. Konigs, *B.* 20, 2516).

Dehydroquiniene $C_{20}H_{20}N_2O$. Formed by boiling quiniene-di-bromide with alcoholic KOH. Colourless crystals (with 3aq). V. sol. alcohol and ether, nearly insol. water. Dissolves in very dilute H_2SO_4 with a strong green-blue fluorescence. Gives the quinine reaction with chlorine and ammonia (Comstock a. Konigs, *B.* 20, 2517).

Quinicine $C_{20}H_{24}N_2O_2$. [60°]. $[\alpha]_D = +44°$ (in a 2 p.c. chloroform solution). Occurs in cinchona bark (Howard, *C. J.* 24, 61; 25, 101). Formed by heating the sulphate of quinine or quinidine with H_2SO_4 at 130° (Pasteur, *C. R.* 37, 110; Hesse, *A.* 178, 245). Formed also by heating quinine or quinidine with glycerin at 200° (Hesse, *A.* 166, 277). Oil, which slowly solidifies. Sl. sol. water, v. sol. alcohol and ether. Its alcoholic solution is alkaline to litmus. Cl and NH_3 give a green colour. Its solution in dilute H_2SO_4 is not fluorescent.

Salts.—$B'H_2PtCl_6$ 2aq. — B'HI aq. — $B'_2H_2SO_4$ 3aq. Oxalate $B'_2H_2C_2O_4$ 9aq. S. ·4 at 16°.—Acid tartrate $B'C_4H_6O_6$ 6aq. [100°]. Sulphocyanide B'HSCy ½aq.

Apoquiniene $C_{18}H_{17}NO_2$. *Apoconquinine.* [246°]. Formed by heating quiniene with aqueous HBr (S.G. 1·5) at about 180° (Comstock a. Konigs, *B.* 18, 1226). Colourless crystals. V. sol. alcohol, sl. sol. water, ether, and benzene. It dissolves in aqueous acids and alkalis, forming yellow solutions. The sulphate is sparingly soluble. The hydrobromide forms small yellow crystals.

Cupreine $C_{19}H_{22}N_2O_2$. [198°]. (Paul a. Cownley, *Ph.* [3] 15, 221; Hesse, *A.* 230, 55). Occurs in cuprea bark. The crude quinine sulphate from such bark is dissolved in aqueous H_2SO_4, excess of NaOH is added, and the ppd. quinine shaken out with ether. The aqueous liquid is warmed and neutralised with H_2SO_4. Cupreine sulphate then separates (Hesse, *A.* 226, 240; 230, 57).

Properties.—Concentric prisms, containing 2aq (from ether). From alcohol it separates in the dry form. V. sl. sol. ether or chloroform, more sol. alcohol. The alcoholic solution is alkaline to litmus, gives a dark reddish brown colour with Fe_2Cl_6, and a deep green with chlorine water, followed by ammonia. The solution in dilute H_2SO_4 does not fluoresce, but gives with NH_3 a pp. slightly soluble in excess of NH_3, and easily soluble in NaOH. Ether extracts the base from the ammoniacal solution, but not from the solution in NaOH. It rotates light to the right almost as strongly as quinine. Its neutral salts form yellow solutions; its acid salts are colourless. HCl (S.G. 1·125) at 140° converts cupreine into apoquinine, no MeCl being evolved.

Salts.—(Hesse, *A.* 230, 59.) $B''_2H_2SO_4$ 6aq. $B''H_2SO_4$ aq. — $B''HCl$ aq. — $B''(HCl)_2$. — $(B''HCl)_2PtCl_4$ 4aq. — $B''(HCl)_2PtCl_4$ aq. — $B''_2H_4C_6O_6$ 2aq. The base combines with NaOH and KOH (1 mol.), but not with NH_3. It also forms calcium, lead, and silver compounds.

Diacetyl derivative $C_{19}H_{20}Ac_2N_2O_2$ [88°]. Salt.—$C_{19}H_{20}Ac_2N_2O_2H_2PtCl_6$ 3aq.

Mono-methylo-compounds.—$B''MeI$. Is thrown down on adding MeI to alcoholic cupreïne solution. Colourless needles, very sparingly soluble in alcohol or water, insoluble in ether. Very soluble both in acids and alkalis.—$B''MeCl$.—$B''MeCl.HCl.PtCl_4$ 2aq. $(B''Me)_2SO_4$. On adding baryta to a solution of the methylo-sulphate, and evaporating the filtrate, the hydroxide, $(B''Me)OH$, remains as a yellow amorphous residue. It has a bitter taste, is insoluble in ether, but very soluble in water. With a little bleaching-powder and ammonia it gives a green colour; if more bleaching-powder is used the colour is red.

Di-methylo-compounds $B''2MeI$ 5aq forms orange plates (from water), soluble in acids, alkalis, and alcohol (though not in water). The corresponding hydroxide is only known in solution.

Hydrocupreine $C_{19}H_{24}N_2O_2$. [169°]. Formed by heating hydroquinine sulphate with HClAq (S.G. 1·125) (Hesse, *A.* 241, 279). Microcrystalline powder (containing 2aq). Alkaline to litmus. A solution of its sulphate does not fluoresce.—$B'_2H_2SO_4$: small needles, v. sl. sol. water and alcohol.—$B'_2C_4H_6O_6$ 2aq.—$B'H_2Cl_2$ aq. —$B'H_2PtCl_6$.

Homoquinine. This substance, obtained from *China cuprea* (the bark of *Remijia pedunculata*) (Howard a. Hodgkin, *C. J.* 41, 66), is also formed by adding sodium cupreine to quinine hydrochloride (Hesse, *A.* 230, 70). It is therefore a molecular compound of quinine and cupreine, $C_{20}H_{24}N_2O_2,C_{19}H_{22}N_2O_2$,4aq.

Cuscamine. [218°]. An alkaloid in the bark of *Cinchona Pelletierana* (Hesse, *A.* 200, 304). Prisms; v. sol. ether, m. sol. alcohol.

Cusconine $C_{23}H_{26}N_2O_4$2aq. [110°]. S. (ether) 3 at 18°. $[\alpha]_D = -54°$ (in a 2 p.c. alcoholic solution). Occurs together with aricine in the bark of *C. cuprea* (Hesse, *A.* 185, 320; Paul a. Cownley, *Ph.* [3] 12, 497). Plates (containing 2aq) (from ether). Its acid solutions do not fluoresce. Lævorotatory. Conc. HNO_3 turns it dark green. $B'HHgCl_3$2aq. — $B'_2H_2PtCl_6$5aq: amorphous.— $B'_2H_2SO_4x$aq. —B'HSCy 2aq: yellow powder.

Concusconine $C_{23}H_{26}N_2O_4$aq. [144°]. When dry [c. 208°]. $[\alpha]_D = +40·8°$ at 15° in 2 per cent. alcoholic solution. In bark of *Remijia Purdieana* (cuprea bark) (O. Hesse, *A.* 225, 234). Monoclinic crystals (containing aq). Sl. sol. alcohol, but ppd. by water from that solution. V. sol. benzene, ether, and chloroform; sl. sol. petroleum. Its alcoholic solution is neutral to litmus. At 150° it partly changes to an amorphous variety. It forms no acetyl derivative with Ac_2O. Conc.

HNO_3 added to its solution in acetic acid or HCl gives a splendid dark-green colour. Conc. H_2SO_4 forms a blue-green solution, turned olive-green on warming.

Salts.—Mostly gelatinous.—$(B'HCl)_2PtCl_4$ 5aq.—$B'_2H_2C_2O_4.B'_2H_2SO_4$. Prisms.

(α)-*Methylo-iodide* B'MeI. Crystalline powder: hardly sol. alcohol, sol. boiling water. From it may be obtained: B'MeCl, needles; $(B'MeCl)_2PtCl_4$, amorphous; $(B'Me)_2SO_4$; and B'MeOH, which when dry melts at [202°].

(β)-*Methylo-iodide* B'MeI. Gelatinous. V. sol. alcohol. From it may be obtained: B'MeCl, amorphous; $(B'MeCl)_2PtCl_4$5aq, amorphous; $(B'Me)_2SO_4$; and B'MeOH $2\frac{1}{2}$aq.

Cusconidine. An amorphous alkaloid in Cusco bark (Hesse, *A.* 200, 303).

Concusconidine $C_{21}H_{26}N_2O_4$. [124°]. A slightly dextrorotatory amorphous alkaloid, said to occur in cuprea bark (Hesse, *B.* 16, 62).—$B''_2H_2PtCl_6$.

Hydroquinine $C_{20}H_{26}N_2O_2$. [168°]. $[\alpha]_D = -142{\cdot}2°$ ($p = 2{\cdot}4$ in 95 p.c. alcohol at 20°, but $[\alpha]_D = -227{\cdot}1°$ in dil. HCl. Discovered by Hesse (*B.* 15, 856) in mother-liquors of quinine sulphate.

Preparation (Hesse, *A.* 211, 255).—The mother-liquor from quinine monosulphate is treated with successive quantities of sulphuric acid until a neutral salt is obtained containing over 30 p.c. of hydroquinine sulphate. The quinine is then removed with $KMnO_4$, and after neutralisation with NaOHAq the hydroquinine is extracted with ether, benzene, or chloroform.

Properties.—Can be obtained by neutralising the solution in dilute acid with NaOHAq as an amorphous pp. having the composition $C_{20}H_{26}N_2O_2$ 2aq. Crystallises from chloroform in concentric grouped needles. V. sol. alcohol, chloroform, ether, benzene, and CS_2, m. sol. ammonia, sl. sol. water, insol. NaOHAq. Solution in dilute H_2SO_4 shows blue fluorescence, and gives the same reactions as quinine with Cl and ammonia, but decolourises $KMnO_4$ very slowly. Alkaline reaction, bitter taste. Heated with HCl it yields hydrocupreine.

Salts.—$B'_2H_2SO_4$6aq: short white prisms; v. sol. alcohol and hot water, sl. sol. cold water, insol. ether. S. ·287 at 15°. $[\alpha]_D = -193{\cdot}4°$.—$B'H_2SO_4$ 3aq: long thin needles; v. sol. water and alcohol, m. sol. acetone. Heated to 120° it gives off water, and to 140° yields hydroquinicin sulphate.—$B'_2H_2S_2O_2$2aq.—B'HCl 2aq: long flat prisms; v. sol. water and alcohol, insol. ether.—$B'_2PtCl_6H_2$ 3aq: yellow amorphous pp.; v. sl. sol. water and alcohol.—$B'PtCl_6H_2$ 2aq.—$B'2AuCl_4H$ 2aq(?): yellow amorphous pp.—$B'2HClHgCl_2$: small colourless flat needles.—B'BrH 2aq.—$B'(BrH)_2$ 3aq: B'IH: oil, becoming solid but not crystallising.—$B'(IH)_2$ 4aq: shining yellow needles.—$B'H_2I_6$ $x$aq: metallic, dichroic flat needles.—B'HCNS: a resin; m. sol. water.—$B'C_2H_4O_2$5aq. [100°]: small colourless needles; v. sol. water and alcohol.—**Benzoate** $B'C_7H_6O_2$: small needles; v. sol. alcohol, sl. sol. water.—**Salicylate** $B'C_7H_6O_3$: small colourless needles; v. sl. sol. cold water, m. sol. hot water, v. sol. alcohol.—**Piperonylate** $B'C_8H_6O_4$.—$B'_2C_2O_4H_2$ 6aq: long shining needles; insol. ether, v. sol. hot, sl. sol. cold, water, v. sol. alcohol. S. ·213 at 15°.—$B'_2C_4H_6O_6$ 2aq: thick colourless prisms; m. sol. hot water, alcohol, v. sol. chloroform-alcohol, sl. sol. water. S. ·183 at 17°. $[\alpha]_D = -176{\cdot}35°$ (*cf. Ph.* [3] 16, 1025).—**Citrate** $B'_3C_6H_8O_7$ 10aq: small white needles; v. sol. boiling, sl. sol. cold, water.—$B'_2PO_4H_3$7aq: small white needles; sl. sol. water.—$B'_3(AsO_4H_3)_2$ 10aq: long white needles.—$B'_2CrO_4H_2$6aq: long golden needles; m. sol. hot, sl. sol. cold, water, v. sl. sol. chloroform.

Combinations.—1. With **cupreïne** $C_{20}H_{26}N_2O_2.C_{19}H_{22}N_2O_2$2aq; long shining needles grouped concentrically.—2. With **quinidine** $C_{20}H_{26}N_2O_2.C_{20}H_{24}N_2O_2$ $2\frac{1}{2}$aq; white needles.—3. With **anethol** $(C_{20}H_{26}N_2O_2)_2C_{10}H_{12}O$2aq. Large shining dimetric prisms. V. sol. hot alcohol, ether; sl. sol. cold alcohol; insol. water. Decomposes at 120° into hydroquinine, anethol, and water.—4. Also forms compounds with hydroquinidine, cinchonidine, hydrocinchonidine, and homocinchonidine, but not with cinchonine or hydrocinchonine.

Methylo-compounds B'MeIEtOH. Pale yellow prisms. [218°]. V. sol. hot, m. sol. cold alcohol, insol. water.—B'MeCl 2aq [168°].—$B'MeHPtCl_6$ 2aq: orange-red needles.—$B'_2Me_2PtCl_6$: pale-yellow needles; m. sol. alcohol and water.—B'MeOH: resin; insol. ether and chloroform; v. sol. alcohol and water. Absorbs CO_2.

Acetyl derivative $C_{20}H_{25}N_2O_2Ac$. [c. 40°]. V. sol. ether, alcohol, benzene, acetone, and acids; sl. sol. water, and NH_3. $[\alpha]_D = -73{\cdot}9°$. in 3 molecules HClAq $p = 3$, $t = 15°$.—$(C_{20}H_{25}AcN_2O_2)PtCl_6H_2$ 2aq: powdery pp.; sl. sol. dil. HCl and water.—$(C_{20}H_{25}AcN_2O_2)_2SO_4H_2$ 9aq: long needles; v. sol. hot water, alcohol, sl. sol. cold water, insol. ether.

Sulphonic acid.—Strong H_2SO_4 at ordinary temperatures forms hydroquinine sulphonic acid $C_{20}H_{25}N_2O_2.SO_3H$ aq [239°]; insol. ether, chloroform; sl. sol. NH_3 and NaOHAq.—$(C_{20}H_{25}N_2O_2.SO_3H)PtCl_6H_2$ 8aq: pale-yellow needles.

Hydroquinicine $C_{20}H_{26}N_2O_2$. Formed by fusing hydroquinine sulphate at 140° (Hesse, *A.* 241, 273). Yellow resin. V. sol. ether, alcohol, chloroform and dilute acids. Solution in dilute H_2SO_4 is intensely yellow, addition of chlorine-water and ammonia gives a yellowish green colouration. More easily acted on by $KMnO_4$ than hydroquinine.—**Salts**.—**Neutral sulphate**; white needles, v. e. sol. alcohol and water.—$B'PtCl_6H_2$ aq: pale yellow flocculent pp. changing to orange-coloured crystals insol. water, sl. sol. dilute HCl.

Hydroquinidine $C_{20}H_{26}N_2O_2$. *Hydroconquinine.* [167°]. Occurs in crude quinidine, and obtained therefrom by treatment in acid solution with $KMnO_4$ which does not attack hydroquinidine (Forst a. Bohringer, *B.* 14, 1954; 15, 519, 1656; Hesse, *B.* 15, 854). Needles or tables. M. sol. ether, v. sol. alcohol and chloroform. The alcoholic solution is alkaline to litmus. Its solution in dilute H_2SO_4 shows blue fluorescence. It is dextrorotatory. Chlorine-water and NH_3 give a green colour. Chromic mixture forms quinic acid.

Salts.—B'HCl: soluble prismatic tables.—B'HBr: plates, sl. sol. cold water.—$B'H_2PtCl_6$ 2aq. $B'_2H_2SO_4$12aq.—B'HI.—$B'H_2I_2$3aq: large orange soluble crystals.—**Tartrate** $B'_2C_4H_6O_6$ 2aq: glistening soluble prisms.—**Acid tartrate**

$B'C_4H_8O_6$ 3aq: thin white needles, sl. sol. cold water.—Benzoate $B'C_7H_6O_2$: colourless tables. —Salicylate $B'C_7H_6O_3$: six-sided tables.

Hydrocinchonidine. Identical with CINCHAMIDINE (*v.* CINCHONA BASES).

Homocinchonidine $C_{19}H_{22}N_2O$. [206°]. S. (alcohol) 4·9 at 13°; S. (ether) ·46 at 15°. $[\alpha]_D = -107^\circ$ in a 2 p.c. alcoholic solution at 5°. Occurs in very small quantity in many cinchona barks, especially that of *C. rosulenta* (Hesse, *B.* 14, 46, 1891; *A.* 205, 203; 207, 310; *cf.* Skraup, *A.* 199, 365). Obtained by recrystallisation of crude cinchonidine sulphate. Prisms or plates. Lævorotatory. Its alcoholic solution is alkaline to litmus. Its solution in H_2SO_4 does not fluoresce. It gives no green colour with Cl and NH_3. Conc. HCl at 150° gives apocinchonidine and apocinchonidine chlorohydride. $KMnO_4$ forms formic acid and cinchotenidine.

Salts.—B'HCl aq.—B'HCl 2aq. $[\alpha]_D = -139^\circ$. —$B'H_2PtCl_6$ aq.—$B'_2H_2PtCl_6$ 2aq.—$B'HNO_3$ aq.—$B'H_2S_2O_3$ 2aq. S. ·5 at 13°.—$B'_2H_2SO_4$ 6aq. S. 1·15 at 22°. $[\alpha]_D = -138^\circ$ in an 8 p.c. aqueous solution.—B'HSCy. — Tartrate $B'C_4H_6O_6$ 2aq. S. ·075 at 10°.—Quinate $B'C_7H_{12}O_6$.—Phenyl sulphate B'_2HSO_4Ph 5aq.

Acetyl derivative $C_{19}H_{21}AcN_2O$. $[\alpha]_D = -34^\circ$ in a 2 p.c alcoholic solution at 15°.—$B'H_2PtCl_6$ 2aq.—$B'(HAuCl_4)_2$ aq.

Cinchotenidine $C_{18}H_{20}N_2O_3$. [256° cor.]. S. (alcohol) ·13 at 78°. Formed by oxidation of homocinchonidine or cinchonidine (Skraup a. Vortmann, *A.* 197, 235; Hesse, *B.* 14, 1892). Needles or prisms (containing 3aq). Its solution in dilute H_2SO_4 does not fluoresce. Its solution in HClAq is lævorotatory. $[\alpha]_D = -201^\circ$.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$ 2½aq; v. e. sol. water.

Diconquinine $C_{40}H_{46}N_4O_3$. An amorphous alkaloid occurring in most cinchona barks (Hesse, *B.* 10, 2155). Is the chief constituent of commercial 'quinoidine.' Dextrorotatory. Gives a green colour with Cl and NH_3. The solution in dilute H_2SO_4 is fluorescent. Its salts are amorphous.

Paricine $C_{16}H_{18}N_2O$. [130°]. Found by Winkler (*B. J.* 27, 338) in a false cinchona bark. Occurs in the bark of *C. lutea*, and *C. succirubra* of Darjeeling (Hesse, *A.* 166, 263; *Ph.* [3] 9, 839). The aqueous solution of the mixed sulphates of quinine, cinchonine, paricine, &c. is treated with conc HNO_3 which throws down paricine nitrate. Paricine may also be ppd. from the mixed sulphates by adding Na_2CO_3 to feeble alkaline reaction. Yellow powder. V. e. sol. alcohol and ether. The alcoholic solution is alkaline to litmus and is inactive.—$B'_2H_2PtCl_6$ 4aq.

Javanine. Occurs in the bark of *C. Calisaya javanica* (Hesse, *B.* 10, 2162). Plates (from water). Its solution in dilute H_2SO_4 is intensely yellow.

CINCHONIC ACID *v.* QUINOLINE-(*Py.* 1)-CARBOXYLIC ACID.

CINCHONIDINE $C_{19}H_{22}N_2O$. [200°] (H.); [210° cor.] (S. a. V.). S. ·06 at 10°. S. (ether) ·53 at 15°; S. (97 p.c. alcohol) 6·1 at 13°. $[\alpha]_D = -70^\circ$ in a 4 p.c. solution in alcohol-chloroform. Discovered by Winkler (*Repert. Pharm.* [2] 48, 384; 49, 1) and occurs in most cinchona barks (Leers, *A.* 82, 147; Pasteur, *C. R.* 37, 110; *C. J.* 6, 275; Bussy a. Guibourt, *J. Ph.* [3] 22, 401; Hesse, *A.* 135, 333; 166, 240; 176, 203; 181, 50; 182, 160; 205, 196; 207, 310; Skraup a. Vortmann, *A.* 197, 226). Separated from quinine and other bases by repeated extraction with ether. It is then converted into the hydrochloride and ppd. by hydrosodic tartrate. The base, liberated from the tartrate, is then crystallised from alcohol.

Properties.—Gives no green colour with chlorine water and ammonia. Its solution in dilute H_2SO_4 does not fluoresce.

Reactions.—1. HNO_3 gives the same products as with cinchonine. CrO_3 does the same.—2. H_2SO_4 at 130° or glycerin at 200° converts it into cinchonicine.—3. Heating with HCl gives apocinchonidine, (β)-cinchonidine, and apocinchonidine chloro-hydride.—4. Oxidised by $KMnO_4$ to pyridine tri-carboxylic acid. [257°] (Ramsay a. Dobbie, *C. J.* 35, 189).—5. PCl_5 converts it into cinchonidine-chloride $C_{19}H_{21}N_2Cl$, which by boiling with alcoholic KOH gives cinchene $C_{19}H_{20}N_2$, and this by heating with HCl at 220° is converted into apocinchene $C_{18}H_{17}NO$ (Comstock a. Konigs, *B.* 17, 1986).

Salts.—B'HCl aq: monoclinic crystals. S. 3·3 at 10°. S. (ether) ·3 at 10°. Lævorotatory. $[\alpha]_D$ varies from −24° (in chloroform) to −152° (in dilute HClAq).—B'HCl 2aq: prisms.—$B'H_2Cl_2$ aq.—$B'H_2HgCl_4$: scales.—$B'H_2PtCl_6$ aq. $B'H_2PtCl_6$ 2aq. — $B'H_2AuCl_4$. — $B'H_2I_2$ aq. — $B'HNO_3$ aq. S. 1·4 at 10°.—$B'_2H_2SO_4$ 6aq. S. 1 at 12°; 1·5 at 22°: prisms. $[\alpha]_D = -111^\circ$ (in water).—$B'H_2SO_4$ 5aq: striated prisms, v. sol. water and alcohol. — $B'(H_2SO_4)_2$ 2aq: short prisms, sl. sol. cold water.—$B'H_2S_2O_3$ 2aq. S. ·45 at 10°.—$B'_{12}(H_2SO_4)_9H_8I_{32}$ 8aq: golden plates (Herapath, *C. J.* 9, 130; Jorgensen, *J. pr.* [2] 14, 371).—$B'_4(H_2SO_4)_2H_3I_9$ 4aq.—$B'_8(H_2SO_4)_5H_6I_{18}$ 6aq. $B'_2H_2SO_4HI_5$ aq. — $B'_{12}(H_2SeO_4)_9H_8I_{32}$ 8aq. — $B'_2H_2SeO_4HI_5$ aq. — $B'_3(H_3PO_4)_2$ 12aq.— $B'_2(H_3PO_4)_2HI_5$.—$B'_2(H_3AsO_4)_2$.—B'HSCy. S. ·5 at 20°. Acetate B'HOAc aq. — Benzoate $B'C_7H_6O_2$. S. ·3 at 10°.—Oxalate $B'_2H_2C_2O_4$ 6aq. S. ·4 at 10°. $[\alpha]_D = -99^\circ$. — $B'_2H_2C_2O_4H_2I_6$. — Succinate $B'_2C_4H_6O_4$ 2aq. S. ·17 at 10°. Tartrate $B'_2C_4H_6O_6$ 2aq: crystalline pp.; insol. aqueous sodio-potassium tartrate. S. ·04 at 10° (tartrate of cinchonine is far more soluble). — $B'_2C_4H_6O_6HI_4$. — Acid tartrate $B'(C_4H_6O_6)_2$ 3aq. — Salicylate $B'C_7H_6O_3$. S. ·13 at 18°.

Combinations with Phenol.—B'_2HOPh. Prisms. Formed by mixing alcoholic solutions of phenol and cinchonidine.—$B'_2(HOPh)_3$: unstable crystals.—B'HClHOPh aq: crystalline grains, formed by adding phenol to an aqueous solution of cinchonidine hydrochloride.—B'_2SO_3HOPh 5aq. Formed by mixing hot aqueous solutions of phenol and cinchonidine sulphate. Prisms. S. ·235 at 15°.

Acetyl derivative $C_{19}H_{21}AcN_2O$. [42°]. $[\alpha]_D = -38^\circ$ in a 2 p.c. alcoholic solution at 15°; $= -81^\circ$ in a solution in dilute HCl. Brittle mass.—$B'H_2PtCl_6$ 2aq.—$B'(HAuCl_4)_2$ aq.

Methyl-cinchonidine $C_{19}H_{21}MeN_2O$. [76°]. From the iodide by treatment with aqueous KOH (Stahlschmidt, *A.* 90, 218; Claus a. Bock, *B.* 13, 2191; Hesse, *B.* 14, 45). Needles or tables (containing aq). Its salts are mostly deliquescent. Iodide $C_{19}H_{21}MeN_2OHI$. [248°]. From cinchonidine and MeI. Slender needles.—

Chloride $B'HCl$. [158°]. Slender needles (containing aq). - $B'H_2PtCl_6 3aq$.

Methylo-iodide $C_{19}H_{21}MeN_2O.MeI\,2aq$: crystals.

Methylo-di-iodide $C_{19}H_{21}MeN_2O.HI.MeI$: large prisms.

Ethyl - cinchonidine $C_{22}H_{28}N_2O$. [90°]. Colourless needles. V. sol. alcohol and ether, insol. water. Prepared by the action of aqueous KOH on the iodide (Claus a. Dannenbaum, *B.* 13, 2189).

Salts.—$B'HCl\,3aq$: cubes; v. sol. water and alcohol (Howard, *C. J.* 26, 1181; Claus, *B.* 14, 1922). Lævorotatory.—$B'HBr\,aq$.—$B'HI$. [261°] From cinchonidine and EtI. Needles. $B'HI_3$.- $B'HCy$. [140°]. Slender needles, v. sol. water (Claus a. Merck, *B.* 16, 2745).—$B''H_2Cl_2PtCl_4\,aq$: crystalline pp.

Methylo-iodide BMeI. Colourless needles. Decomposes at 257°.

Ethylo-iodide BEtI. Resembles the methylo-iodide; on treatment with KOH it gives a di-ethyl-cinchonidine.

Ethylo-di-iodide $C_{19}H_{21}EtN_2OHEtI_2aq$. [255°]. Golden crystals.

Isoamyl - cinchonidine $C_{19}H_{21}(C_5H_{11})N_2O$. Resin.—$B'H_2PtCl_6\,x\text{aq}$ (Claus a. Weller, *B.* 14, 1922).

Di-bromo-cinchonidine $C_{19}H_{20}Br_2N_2O$. From cinchonidine in CS_2 and Br (Skalweit, *A.* 172, 103).—$B'H_2Br_2$: needles, v. sol. alcohol.

Di-oxy-cinchonidine $C_{19}H_{20}(OH)_2N_2O$. From the preceding by long boiling with alcoholic KOH (S.). Ramified crystals. -$B'_2H_2SO_4 2aq$: plates.—$B'H_2SO_4$.- -$B'H_2PtCl_6$.

Apocinchonidine $C_{19}H_{22}N_2O$. [225°]. $[\alpha]_D = -129°$ in a $\frac{1}{5}$ p.c. alcoholic solution at 15°. Formed by heating cinchonidine with HCl (6 pts. of S.G. 1·105) at 150° (Hesse, *A.* 205, 327). Small plates (from alcohol). Lævorotatory. Its acid solutions do not fluoresce.- -$B'H_2PtCl_6 2aq$.

Acetyl derivative $C_{19}H_{21}AcN_2O$. $[\alpha]_D = -62°$ in a 2 p.c. alcoholic solution at 15°.—$B'H_2PtCl_6 2aq$.—$B'(HAuCl_4)_2\,aq$.

Apocinchonidine chlorohydride $C_{19}H_{24}ClN_2O$. [200°]. $[\alpha]_D = -142°$ in a 2 p.c. solution of dilute HCl (containing 3HCl). From apocinchonidine and fuming HCl at 150° (Zorn, *J. pr.* [2] 8, 283; Hesse, *A.* 205, 316). Plates (from alcohol). Lævorotatory. $B'H_2Cl_2$. $B'H_2PtCl_6 2aq$.

Acetyl derivative $C_{19}H_{22}AcClN_2O$. [150°]. Prisms (from ether). Lævorotatory.—$B'H_2PtCl_6 2aq$.

(β)-Cinchonidine $C_{19}H_{22}N_2O$. [207°]. $[\alpha]_D = -181°$ in a $1\frac{1}{4}$ p.c. solution in dilute HCl at 15°. Formed, together with apocinchonidine, by heating cinchonidine with HCl (S.G. 1·105) at 140°. Separated from apocinchonidine through the insolubility of its tartrate (Hesse, *A.* 205, 327). Short prisms or plates. Lævorotatory. The neutral **tartrate** is v. sl. sol. water. By heating with HCl for a long time it changes to apocinchonidine.—$B'H_2PtCl_6\,aq$.

Iso-cinchonidine $C_{19}H_{22}N_2O$. [235°]. Formed by dissolving cinchonidine in conc. H_2SO_4 (Hesse, *A.* 243, 149). Colourless plates. V. sl. sol. ether, v. sol. alcohol and chloroform.

CINCHONINE $C_{19}H_{22}N_2O$. [236°] (when slowly heated); [248°-252°] (when quickly heated) (Hesse); [260°] (Skraup). $[\alpha]_D = 226°$ in a 1 p.c. alcoholic solution; $= 255°$ in dilute H_2SO_4; $= 268°$ in a 10 p.c. solution containing 1 mol. H_2SO_4 at 15° (Hesse; *cf.* Oudemans, *Ar. Néerl.* 10, 193). S. ·262 at 10°; S. (alcohol of S.G. ·852) ·71 at 10°; S. (ether) ·27 at 10°; S. ($CHCl_3$) ·28. Occurs, together with quinine, in most of the true cinchona barks (Fourcroy, *Ann. Chim.* 8, 113; 9, 7; Vauquelin, *Ann. Chim.* 59, 30, 148; Gomez, *Edinb. Med. and Surg. Journal*, 1811, 420; Pfaff, *Schw. J.* 10, 365; Pelletier a. Caventou, *A. Ch.* 15, 291, 337; Pelletier a. Dumas, *A. Ch.* 24, 169; Gerhardt, *Revue scient.* 10, 886; *Traité*, 4, 105; Laurent, *A. Ch.* [3] 19, 363; Regnault, *A. Ch.* 68, 113; *A.* 26, 15; Liebig, *A.* 26, 49; Hlasiwetz, *A.* 77, 49; Weidel, *A.* 173, 76; Hesse, *A.* 122, 226; 135, 326; 166, 217; 205, 211; Skraup, *A.* 197, 353; Oudemans *A.* 182, 44).

Preparation.—The bark is extracted with dilute acid. The alkaloids are ppd. by lime, Na_2CO_3, or NaOH, and crystallised from alcohol (85 p.c.). Cinchonine crystallises out before quinine, unless the quantity of the latter present be relatively large, in which case a portion of the quinine is first removed by crystallisation of the sulphates. Quinine may be separated from cinchonine by ether, which dissolves quinine most readily.

Properties.—Prisms (from alcohol). When ppd. by ammonia from aqueous solutions of its salts it is amorphous, but rapidly becomes crystalline. Tastes bitter. Its solutions are alkaline to litmus and dextro-rotatory. Its solution in dilute H_2SO_4 does not fluoresce. It does not give a green colour with chlorine-water and ammonia. It gives a yellow pp. with chloride of iodine.

Reactions.—1. Oxidised by $KMnO_4$ to pyridine tri-carboxylic acid (Dobbie a. Ramsay, *C. J.* 35, 189). 10 g. cinchonine dissolved in 4·5 g. H_2SO_4, diluted with water to 100 c.c., and treated gradually with 285 c.c. of a 5 p.c. solution of $KMnO_4$ gives cinchotine, cinchotenine, and quinoline carboxylic acid (Skraup, *A.* 201, 291). In the syrupy oxidation products of cinchonine are a monobasic acid $C_8H_{13}NO_4$, a base $C_9H_{17}NO_2$, yielding an ethyl-pyridine identical with that of Wyschnegradsky, C_9H_7NO, identical with Schmideberg a. Kretschy's base kynurine, and an amorphous product $C_{13}H_{14}NO_2$ (Skraup, *M.* 7, 517, 518). Alkaline $KMnO_4$ gives off 41 p.c. of the nitrogen as NH_3 (Hoogewerff a. Van Dorp, *A.* 204, 90).—2. H_2SO_4 and PbO_2 give a red substance, cinchonetin (Marchand, *J. Chim. Med.* 10, 362). 3. Boiling HNO_3 (S.G. 1·4) forms quinoline carboxylic (cinchonic) acid, quinolic acid $C_9H_6N_2O_6$, pyridine dicarboxylic (cinchomeronic) acid, pyridine tri-carboxylic acid and a base $C_{16}H_{18}N_2O_5$ (Weidel, *A.* 173, 76).—4. CrO_3 gives quinoline carboxylic acid and some formic acid, which perhaps indicates a methoxyl group (Skraup, *A* 201, 291).—5. PCl_5 converts it into cinchonine-chloride $C_{19}H_{21}N_2Cl$ [52°], which by boiling with alcoholic KOH gives cinchene $C_{19}H_{20}N_2$, and this by heating with HCl at 220°-230° is converted into apocinchene $C_{18}H_{17}NO$ by splitting off MeCl and NH_3 and taking up H_2O (Comstock a. Königs, *B.* 17, 1984).—6. Treatment with CuO and KOH gives quinoline and a resin whence oxidation produces pyridine dicarboxylic acid (Wyschnegradsky, *B.* 13, 2318). 7. Distillation with solid *potash* yields methylamine, (α) and (β) di-methyl-pyridine, (α) and (β) tri-methyl-pyridine, quinoline, and quinoline tetrahydride (Oechsner de Coninck, *A. Ch.* [5] 27, 453; *C. R.* 94, 87).—8. Aqueous KOH gives quinoline and a solid body (Butlerow, *J. R.* 10, 244); in presence of superheated steam KOH forms also methyl-quinoline (Krakau, *Bl.* [2] 45, 248).—9. H_2SO_4 and a little water at 130° forms the isomeric cinchonicine; this body is also formed by fusing the acid sulphate of cinchonine. According to Jungfleisch a. Léger (*C. R.* 105, 1255) pure sulphate of cinchonine dissolved in a mixture of equal parts of water and pure H_2SO_4 yields a colourless liquid, which when heated for some time to 120° and then rendered alkaline yields a pp. of six bases: cinchonibine (α_D = +175·8° in a ¾ p.c. alcoholic solution), cinchonifine (α_D = +195°), cinchonigine (α_D = −60°), cinchoniline (α_D = +53°), all having the formula $C_{38}H_{44}N_4O_2$, and the two oxycinchonines (α_D = +182·56° and α_D = +187·14°) of the formula $C_{38}H_{44}N_4O_4$. Fuming H_2SO_4 forms cinchonine sulphonic acid.—10. HCl at 150° forms successively apocinchonine, diapocinchonine, and finally apocinchonine chlorohydride.—11. The product of the action of *sodium ethylate* on cinchonine, after distilling with steam, yields $C_{20}H_{26}N_2$, a heavy reddish yellow viscous oil smelling like quinoline. The constitution of this base is probably $C_{18}H_{21}N_2(C_2H_5)$ (Michael, *Am.* 7, 182).—12. Conc. HBrAq forms apocinchonine bromohydride $C_{19}H_{23}BrN_2O$ and the hydrobromide of that body $C_{19}H_{23}BrN_2OH_2Br_2$ (Skraup, *A.* 201, 324).

Salts.—$B'HCl$2aq. S. 4·2 at 10°; S. (alcohol) 77 at 16°; S. (ether) ·35. $[\alpha]_D$ = 163° in a 1 p.c. aqueous solution; = 212° in presence of 2 mol. HCl (Hesse; *cf.* Schwabe, *J. Ph.* [3] 38, 389).—$B'H_2Cl_2$.—$B'HCl$.—$B'H_2F_2$ ½aq (Elderhorst, *A.* 74, 80).—$B'H_2HgCl_4$: formed by mixing alcoholic solutions of cinchonine hydrochloride and of $HgCl_2$ (Hinterberger, *A.* 77, 201). Needles. — $B'H_2ZnCl_4$ aq. — $B'_2H_6ZnCl_8$ 3aq. — $B'_2H_6ZnCl_8$ aq.—$B'H_2SnCl_4$.—$B'H_2PtCl_6$: amorphous pp. — $B'H_2PtCl_6$ aq. — $B'H_2PtCl_6$ 2aq. — $B'H_2AuCl_5$.—$B'HClO_4$: bulky crystalline tufts (Serullas, *A. Ch.* [2] 45, 278).—$B'(HClO_4)_2$ aq (Bodecker, *A.* 71, 59; Dauber, *A.* 71, 66).—$B'H_2Br_2$.—$B'HI$ aq.—$B'H_2I_2$ aq.—$B'HI_3$ (Bauer, *Ar. Ph.* [3] 5, 289; *cf.* Pelletier, *A. Ch.* [2] 63, 181).—$B'HI_3$ aq [92°]; trimetric brown tables (from alcohol) (Jörgensen, *J. pr.* [2] 3, 145; 15, 82).—$B'HClHI_3I_7$ [97°].—$B'H_2HgI_4$ (Caillot, *B. J.* 10, 193). — $B'_8(H_2SO_4)_6H_6I_{16}$2aq. [140°–145°] (Jörgensen, *J. pr.* [2] 14, 356; *cf.* Herapath, *C. J.* 9, 151).—$B'_4(H_2SO_4)_2H_4I_{14}$.—$B'_2H_2SO_4H_2I_8$. $B'_2H_2SeO_4H_2I_8$. — $B'(H_2C_2O_4)_2H_4I_{14}$. — $B'HIO_3$. Explodes at 120°.—$B'H_4FeCy_6$ 2aq: formed by mixing alcoholic solutions of cinchonine and H_4FeCy_6; lemon-yellow pp.; v. sl. sol. alcohol (Dollfus, *A.* 65, 224).—$B'H_3FeCy_6$ 2aq: orange pp., formed by adding aqueous K_4FeCy_6 to aqueous cinchonine hydrochloride—$B'HSCy$. — $B'HNO_3$ aq: prisms, v. sol. water. $[\alpha]_D$ = 172° Bouchardat).—$B'_2H_2SO_4$ 2aq. Hard prisms. S. 1·5 at 13°. $[\alpha]_D$ = 169° in a 1 p.c. aqueous solution; = 193° in a 1 p.c. alcoholic solution (Hesse). $[\alpha]_D \div [\alpha]_o$ = 1·268 (Grimbert, *J. Ph.* [5] 16, 295). $B'H_2SO_4$ 3aq: trimetric octahedra (Baup, *A. Ch.* [2] 27, 323).—$B'H_2SO_4$ 4aq.—$B'_2H_2S_2O_3$ 2aq.—$B'_2H_2S_2O_3$ aq. — $B'_2H_2Cr_2O_7$. — $B'_2H_3PO_4$ 12aq.—$B'_2H_3AsO_4$ 12aq.—**Oxalate** $B'H_2C_2O_4$ 2aq. S. 1 at 10°. — **Succinate** $B'C_4H_6O_4$ 1½aq. — $B'C_4H_6O_4$ aq. — **Tartrate** $B'_2C_4H_6O_6$ 2aq. S. 3 at 16°. — **Acid tartrate** $B'C_4H_6O_6$ 4aq. S. 1 at 16° (Pasteur, *J.* 1853, 419). — **Lævotartrate** $B'C_4H_6O_6$ aq. S. (alcohol) ·3 at 19°; v. sl. sol. water.—**Citrate** $B'_3C_6H_8O_7$ 4aq. S. 2·1 at 12°. **Acid citrate** $B'_2C_6H_8O_7$ 4aq. S. 1·8 at 15°.—**Urate** $B'C_5H_4N_4O_3$ 4aq.—**Picrate** $B'_2(C_6H_2(NO_2)_3(OH))_3$.—**Benzoate** $B'HOBz$. S. ·6 at 15°.

Acetyl derivative $C_{19}H_{21}AcN_2O$. $[\alpha]_D$ = 114° in a 2 p.c. alcoholic solution. Amorphous; v. sol. alcohol and ether.—$B'H_2PtCl_6$ aq. $B'(HAuCl_4)_2$ aq.

Benzoyl derivative $C_{19}H_{21}BzN_2O$. Amorphous (Schutzenberger, *A.* 108, 351).—$B'H_2PtCl_6$ *x*aq.

Methyl-cinchonine $C_{19}H_{21}MeN_2O$. [71°]. From cinchonine by successive treatment with MeBr and aqueous KOH (Claus, *B.* 13, 2286; *cf.* Stahlschmidt, *A.* 90, 218). Tables (from ether). $B'HBr$ aq. *Cinchonine methylo-bromide.* [248°]. From cinchonine and MeBr. Said not to be identical with the compound of methyl-cinchonine with HBr.—$B'HI$ [254°]. $B'HI_3$ [162°].—$B'H_2PtCl_6$ aq.—$B'HMeBr_2$ [235°]. From cinchonine (1 mol.) and MeBr (2 mols.) at 150°. $B'MeI$. [201°]; needles.—$B'Me_2I_2$. [235°].

Ethyl-cinchonine $C_{22}H_{28}N_2O$. [50°]. Crystalline solid. Prepared by the action of alcoholic KOH on cinchonine-ethylo-iodide (Claus a. Kemperdick, *B.* 13, 2286; *cf.* Howard, *C. J.* 26, 1183).

Salts.—$B'HI$. [260°]. *Cinchonine ethylo-iodide.* White needles. From cinchonine and EtI.—$B'HCl$ aq.—$B'HBr$.—$B'HI_3$ [142°] (Jorgensen, *J. pr.* [2] 3, 152).—$B'H_2Cl_2PtCl_4$ 2aq: yellow pp. The gold double chloride forms small yellow plates.

Ethylo-iodide $B'EtI$. [242°]. From ethyl-cinchonine and EtI. Fine white needles. With KOH it gives di-ethyl-cinchonine. $B'HEtI_2$. *Cinchonine di-ethylo-iodide*: $B'Et_2I_2$ aq. [264°]. Yellow prisms sol. water.

Benzyl-cinchonine $C_{26}H_{28}N_2O$. [117°]. Colourless needles. Prepared by the action of KOH on cinchonine-benzylo-chloride (Claus a. Treupel, *B.* 13, 2294).—$B'HCl$. *Cinchonine benzylo-chloride.* [248°]. From cinchonine and C_7H_7Cl in alcohol. Needles, sol. hot water and alcohol. Ag_2O converts it into $C_{19}H_{21}(C_7H_7)N_2O$ aq said not to be identical with the isomeride got by the action of KOH (Claus).—**Carbonate** [115°].—$B'H_2Cl_2PtCl_4$ 2aq: yellow crystalline pp.

Benzylo-chloride $B'C_7H_7Cl$: [255°]; colourless needles.

Di-chloro-cinchonine $C_{19}H_{20}Cl_2N_2O$. The hydrochloride is ppd. by passing chlorine into a conc. solution of cinchonine hydrochloride (Laurent, *A. Ch.* [3] 24, 302). Crystalline.—$B'H_2Cl_2$. S. (alcohol) 2. — $B'H_2PtCl_6$ aq. — $B'H_2Br_2$.

Bromo-cinchonine $C_{19}H_{21}BrN_2O$. Formed by adding Br to an alcoholic solution of cinchonine (Laurent, *A. Ch.* [3] 24, 302; A. Kopp, *Ar. Ph.* [3] 9, 34). Boiling alcoholic KOH gives 'oxy-cinchonine' [205°].—$B'H_2Cl_2$.

Di-bromo-cinchonine $C_{19}H_{20}Br_2N_2O$. Formed by bromination of cinchonine (Comstock a. Königs, *B.* 17, 1995; *cf.* Laurent, *Compt. chim.*

1849, 311). Colourless crystals containing aq. Sl. sol. alcohol, insol. water. Alcoholic KOH is said by H. Strecker (*A.* 123, 380) to convert it into an oxycinchonine which crystallises from alcohol in plates.

Cinchonine-(α)-di-bromide $C_{19}H_{22}N_2Br_2O$. Formed by the action of bromine upon cinchonine dissolved in a mixture of chloroform and spirit. Crystallises with aq. Boiled with alcoholic KOH it is converted into dehydrocinchonine $C_{19}H_{20}N_2O$. — $C_{19}H_{22}N_2Br_2O,H_2Br_2$ (Comstock a. Konigs, *B.* 19, 2851; 20, 2510).

Cinchonine-(β)-di-bromide $C_{19}H_{22}N_2Br_2O$. Formed at the same time as the preceding, from which it differs in crystallising in an anhydrous condition.

Cinchonine-di-bromide-sulphuric acid. Formed by several hours' standing at the ordinary temperature of a solution of cinchonine-dibromide in 7–8 parts of conc. H_2SO_4. Crystalline solid. Sl. sol. cold water, v. sol. aqueous alkalis, an excess of which precipitates the alkaline salts of the acid. By heating with dilute HBr at c. 130° it is split up again into cinchonine-di-bromide and H_2SO_4 (Comstock a. Konigs, *B.* 19, 2855).

Cinchonine-chloro-hydride $C_{19}H_{23}ClN_2O$. *Hydrochlorcinchonine.* [213°]. Formed by allowing a solution of cinchonine in fuming HCl (saturated at −17°) to stand at the ordinary temperature for several weeks. Colourless crystals (from alcohol). By boiling with alcoholic KOH it yields isocinchonine and a little cinchonine. The *hydrochloride* $C_{19}H_{23}ClN_2O, H_2Cl_2$ crystallises in prisms (Comstock a. Konigs, *B.* 20, 2519).

Cinchonine-bromo-hydride $C_{19}H_{23}BrN_2O$. *Hydrobromcinchonine.* '*Bromcinchonide*' of Skraup. Formed by the action of fuming HBr (saturated at −17°) upon cinchonine at the ordinary temperature or at 100°. Boiled with alcoholic KOH it gives a mixture of cinchonine and isocinchonine. – $C_{19}H_{23}BrN_2O,H_2Br_2$ (Comstock a. Konigs, *B.* 20, 2520).

Cinchonine-chloride $C_{19}H_{21}N_2Cl$. [72°]. Formed by heating the hydrochloride of cinchonine with $POCl_3$ and PCl_5. Trimetric prisms. By boiling with alcoholic KOH it yields cinchene $C_{19}H_{20}N_2$ (Comstock a. Konigs, *B.* 14, 1854; 17, 1984).

Dehydro-cinchonine $C_{19}H_{20}N_2O$. [203°]. Formed by heating cinchonine-di bromide with alcoholic KOH. Colourless needles. Sublimable. V. sol. alcohol, acetone, and chloroform, m. sol. ether and hot benzene, v. sl. sol. ligroin and water. – B'HBr: colourless prisms. – B'HCl: very soluble long silky needles (Comstock a. Königs, *B.* 19, 2856).

Dehydro-cinchonine-bromo-hydride $C_{19}H_{21}BrN_2O$. *Hydrobromdehydrocinchonine. Bromo-cinchonine.* [c. 235°]. Crystalline. Formed by allowing a solution of dehydrocinchonine in very conc. HBr to stand for 8 days at the ordinary temperature (Comstock a. Konigs, *B.* 20, 2524).

'**Dehydrocinchonine-chloride**' $C_{19}H_{19}N_2Cl$. [149°]. Formed by the action of PCl_5 upon dehydrocinchonine. Colourless crystals. V. sol. alcohol, ether, acetone, chloroform, and benzene, nearly insol. ligroin. By boiling with alcoholic KOH it is converted into dehydrocinchene $C_{19}H_{18}N_2$ (Comstock a. Königs, *B.* 19, 2857).

Di-hydro-di-cinchonine $(C_{19}H_{23}N_2O)_2$. [258°]. Formed by treating an acid solution of cinchonine with sodium-amalgam or with zinc and H_2SO_4 (Zorn, *J. pr.* [2] 8, 293; Howard, *C. J.* 26, 1179; Skraup, *B.* 11, 312). Scales (from alcohol).— $B'H_2SO_4$.

Hydrocinchonine $C_{19}H_{24}N_2O$. Formed at the same time as the above. Amorphous. When Cl is passed into an aqueous solution of its chloride there is formed hexa-chloro-hydrocinchonine $C_{19}H_{18}Cl_6N_2O$ and tetra-chloro-dispoline $C_{11}H_7Cl_4N$. HNO_3 converts hydrocinchonine into amorphous tetra-nitro-hydrocinchonine $C_{19}H_{20}(NO_2)_4N_2O$.

Cinchonibine $C_{19}H_{22}N_2O$. [259°]. $[\alpha]_D = 176°$ (in alcohol); = 220° (in HClAq). Insol. water and ether. Alkaline to litmus, but not to phenol-phthalein. — B'MeI. — $B'Me_2I_2$ $1\frac{1}{2}$aq. — B'EtI. – $B'Et_2I_2$ (Jungfleisch a. Léger, *C. R.* 106, 1410).

Cinchonigine $C_{19}H_{22}N_2O$. [128°]. $[\alpha]_D = -60°$. The bases formed from cinchonine by heating with sulphuric acid can be separated by ether. From the ethereal extract HCl pps. cinchonigine hydrochloride and the mother-liquor on concentration, addition of soda and re-extraction with ether gives with HI cinchoniline hydro-iodide. The bases insoluble in ether are 4 in number, and are separated by weak alcohol, in which cinchonibine and cinchonifine are insoluble, while (α) and (β) oxycinchonine dissolve (Jungfleisch a. Leger, *C. R.* 106, 68, 357).

Properties. – Colourless prisms, volatile, distils under reduced pressure, sol. alcohol and dilute HCl. Sl. sol. water; v. sol. chloroform, benzene, and acetone; less sol. dry ether. Probably identical with the base obtained by Caventou a. Girard (*C. R.* 106, 71) by heating cinchonine with oxalic acid and H_2SO_4.

Salts.—B'HCl aq; [213°].—B'2HCl aq.—B'HBr aq.—B'HI aq.—B'2HI aq. – $B'_2C_2H_2O_4$; needles.—$B'C_4H_6O_6$ $3\frac{1}{2}$aq. – B'MeI [253°]; colourless needles. – B'EtI aq [232°]; large prisms from alcohol.—B'EtBr aq. – $B'H_2PtCl_6$ aq (Jungfleisch a. Leger, *C. R.* 106, 357).

Cinchoniline $C_{19}H_{22}N_2O$. [130°]. $[\alpha]_D = +53\ 22°$ in alcohol. Prepared as above. Rhombic prisms, dextrorotatory. Sl. sol. water, v. sol. most solvents. Its aqueous solution is turned blue by litmus and red by phenol-phthalein. Reduced in the cold by $KMnO_4$. Yields the same products as cinchonine on heating.

Salts.—B'HCl 3aq [226°]; v. sol. water $[\alpha]_D = +5°$.—$B'2HClPtCl_4$ aq; yellow prisms. – $B'2HClAuCl_3$ $\frac{1}{2}$aq; prisms.—B'HBr 3aq; prisms, less soluble than the chloride. B'HI aq; B'2HI; B'HCNS aq.

Methyl and ethyl compounds B'MeI [235°]; B'EtI; B'EtBr are all three v. sol. most solvents (Jungfleisch a. Leger, *C. R.* 106, 657).

Cinchotenine $C_{18}H_{20}N_2O_3$. [198°]. $[\alpha]_D = 135°$ in a 2 p.c. alcoholic solution. The chief product of the action of $KMnO_4$ on cinchonine dissolved in dilute H_2SO_4 (Skraup, *B.* 11, 311; *A.* 197, 376). Needles or plates (containing 3aq). Dextrorotatory. Not attacked by cold $KMnO_4$.—$B'H_2PtCl_6$; prisms.—$B'(HAuCl_4)_2$; needles.

Cinchotenicine $C_{18}H_{20}N_2O_3$. [153°]. The sulphate is formed by fusing cinchotenine sulphate

It is feebly dextrorotatory, and forms an amorphous platinochloride.

Cinchonicine $C_{19}H_{22}N_2O$. $(\alpha)_D = 46\cdot5°$ in a 2 p.c. solution in chloroform. Formed by heating the acid sulphate of cinchonine or cinchonidine (Pasteur, *C. R.* 37, 110; Hesse, *A.* 178, 253). Formed also by heating the tartrate or acid tartrate of cinchonine, and by heating cinchonine, cinchonidine, or cinchonine sulphate with glycerin (Howard, *C. J.* 25, 102; Hesse, *A.* 147, 242; 166, 277). Slightly yellowish viscid mass, which becomes a mobile liquid at 50°. V. sol. alcohol and ether. Its alcoholic solution tastes bitter and is alkaline to litmus. Cl and NH_3 give no green colour. Bleaching-powder gives a white pp. in a solution of its hydrochloride (difference from cinchonine and cinchonidine). Dextrorotatory.

Salts. –B'HI: prisms, m. sol. cold water.—$B'_4H_4Cl_4(PtCl_4)_2$ 4aq (?). — $B'H_2PtCl_6$ aq. — Oxalate $B'_2H_2C_2O_4$ 4aq: slender prisms.—Acid tartrate $B'C_4H_6O_6$ aq.

Apocinchonine $C_{19}H_{22}N_2O$. [209°]. $[\alpha]_D = 160°$ in a 1 p.c. alcoholic solution at 16° (Hesse, *A.* 205, 330; Oudemans, *R. T. C.* 1, 173). Formed, together with diapocinchonine, by heating cinchonine with HCl (S.G. 1·125) at 150°. The product is nearly neutralised with ammonia, alcohol is added, and the solution heated to boiling; excess of NH_3 now pps. apocinchonine. Prisms, sl. sol. ether, insol. water.

Salts.—The salts are dextrorotatory, for the neutral salt $[\alpha]_D$ varies from 180° to 215°; for the basic salts from 164° to 176°.—B'HCl 2aq.—$B'H_2PtCl_6$ 2aq. — B'HBr aq. — B'HI aq. — $B'_2H_2SO_4$ 2aq (H.).—$B'_2H_2SO_4$ 3aq (O.).—$B'HClO_3$. $B'HClO_4$ aq. -$B'_2H_2C_2O_4$ 2aq.

Acetyl derivative $C_{19}H_{21}AcN_2O$. $[\alpha]_D = 71°$ in a 2 p.c. alcoholic solution at 15°.—$B'H_2PtCl_6$ 2aq.

Apocinchonine chlorohydride $C_{19}H_{23}ClN_2O$. [197°]. $[\alpha]_D = 211°$ (Oudemans), $= 205°$ (Hesse) in a $\frac{1}{2}$ p.c. alcoholic solution at 16°. Formed by heating cinchonine or apocinchonine with saturated HClAq at 150° (Zorn, *J. pr.* [2] 8, 280; Hesse, *A.* 205, 348). Needles; v. sl. sol. water; sl. sol. ether and alcohol. Dextrorotatory. In the case of the neutral salts $[\alpha]_D$ varies from 215° to 229°; for the basic salts it lies between 192·5° and 195° (O.).—$B'H_2Cl_2$.—B'HCl aq.—$B'H_2Br_2$.—$B'H_2PtCl_6$ 2aq. — $B'_2H_2SO_4$ 3aq. — $B'HNO_3$. — $B'HClO_4$.– $B'HClO_4$ *x*aq.—$B'H_2C_2O_4$ *x*aq.

Acetyl derivative $C_{19}H_{22}AcClN_2O$. $[\alpha]_D = 108°$ in a 2 p.c. alcoholic solution at 15°. Amorphous; v. sol. alcohol and ether.

Apocinchonine bromohydride $C_{19}H_{23}BrN_2O$. From cinchonine and conc. HBrAq at 100° (Skraup, *A.* 201, 324). Scales (from alcohol).—$B'H_2Br_2$: crystals.

Apocinchonicine $C_{19}H_{22}N_2O$. A resinous base, formed by heating apocinchonine acid sulphate at 140°. Inactive; v. sol. alcohol and ether.—$B'H_2PtCl_6$ 2aq.

Di-apocinchonine $(C_{19}H_{22}N_2O)_2$. $[\alpha]_D - 20°$ in a 2 p.c. alcoholic solution at 15°. Formed by the prolonged action of HCl on apocinchonine. Amorphous powder, v. sol. alcohol and ether. Dextrorotatory.—$B'H_2PtCl_6$ 4aq: amorphous.

Acetyl derivative $C_{38}H_{42}Ac_2N_4O_2$. $[\alpha]_D = 26°$ in a 2 p.c. alcoholic solution Yellow amorphous mass.—$B'H_2PtCl_6$ 4aq; amorphous pp.—$B'(HAuCl_4)_4$ 2aq.

Iso-cinchonine $C_{19}H_{22}N_2O$. [127°]. Crystalline. Formed together with cinchonine by boiling cinchonine-chloro- or bromo-hydride ($C_{19}H_{23}ClN_2O$ or $C_{19}H_{23}BrN_2O$) with alcoholic KOH. V. e. sol. alcohol, ether, benzene, chloroform, acetic ether, and CS_2, sl. sol. ligroin, nearly insol. water. It forms easily soluble salts. The zinc double chloride $C_{19}H_{22}N_2O$, $ZnCl_2$, H_2Cl_2 forms small needles (Comstock a. Königs, *B.* 20, 2521). A substance called isocinchonine has also been obtained by Hesse (*A.* 243, 149) among the products of the action of conc. H_2SO_4 on cinchonine.

CINCHOTENICINE *v.* CINCHONINE.

CINCHOTENIDINE *v.* CINCHONINE.

CINCHOTENINE *v.* CINCHONINE.

CINCHOTINE *v.* CINCHONA BASES.

CINCHOVATINE *v.* ARICINE.

CINENE $C_{10}H_{16}$. *Cynene.* (181°–182°). S.G. ^{15} ·854 (Wallach a. Brass, *A.* 225, 309).

Formation.—1. By passing HCl into boiling oleum cinæ (worm-seed oil) or cineol (*cf.* Volckel, *A.* 89, 358).—2. From cineol and BzCl.—3. From $C_{10}H_{18}I_2$ (got from cineol and HI) and aniline.—4. Among the products of the distillation of caoutchouc (when it is called caoutchin).—5. By heating isoprene at 260°.

Properties.—Oil, with pleasant odour of lemon.

Reactions.—1. *Bromine* added to its cold solution in alcohol or ether forms the tetrabromide $C_{10}H_{16}Br_4$ [125°].—2. Conc. H_2SO_4 converts it into cymene, giving off SO_2. P_2S_5 behaves similarly. (*V.* also TERPENES.)

Dihydrochloride $C_{10}H_{18}Cl_2$. [50°].

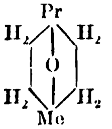
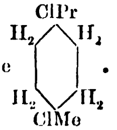
Dihydrobromide $C_{10}H_{18}Br_2$. [64°]. White silky plates. Formed by the action of HBr gas upon worm-seed oil. It is slowly decomposed on standing in contact with alcohol. On heating or by boiling with water or dilute alkalis it loses HBr giving cinene. It decomposes on keeping in the course of several weeks (Hell a. Ritter, *B.* 17, 2609).

Dihydroiodide $C_{10}H_{18}I_2$ [77°]. White felted needles. Formed by the action of gaseous HI upon worm-seed oil. It decomposes on keeping in the course of a few days, and quickly in contact with alcohol. By zinc-dust and water it is reduced to cynene-di-hydride $C_{10}H_{18}$ (Hell a. Ritter, *B.* 17, 2611).

Dihydride $C_{10}H_{18}$ (166°). V.D. = 5 (obs.). Colourless liquid, of ethereal odour. Formed by boiling cinene-di-hydrochloride or cinene-di-hydroiodide with zinc-dust and water (Hell a. Ritter, *B.* 17, 2612).

CINEOL $C_{10}H_{18}O$. (176°). S.G. ^{20} ·927. $\mu_D = 1\cdot458$. V.D. 5·12 (Wallach a. Brass, *A.* 225, 295; 245, 195; Gladstone, *C. J.* 49, 621). The chief constituent of oleum cinæ and of oil of cajeput; occurs also in oil of rosemary (Weber, 238, 89). Liquid, smelling like camphor, inactive. Boiling HNO_3 (S.G. 1·15) forms oxalic acid only.

Reactions.—1. HCl passed into its solution in ligroin forms crystals of $(C_{10}H_{18}O)_2HCl$, a body which is decomposed by water, reproducing cineol, but when heated alone produces cinene: $(C_{10}H_{18}O)_2HCl = 2H_2O + HCl + C_{10}H_{16}$. — 2. HI passed into oleum cinæ ultimately converts it into a crystalline mass of $C_{10}H_{18}I_2$. Crystallised from light petroleum, this forms trimetric tablets: *a*:*b*:*c* = ·7588:1: ·7074 [78·5°]. Alcoholic KOH converts it into cinene.—3. Excess of *Bromine* added at 0° to a solution of cineol in light petroleum forms red crystals of $C_{10}H_{18}OBr_2$. These crystals decompose on keeping, forming cinene tetrabromide and water: $2C_{10}H_{18}OBr_2 = C_{10}H_{16}Br_4 + 2H_2O + C_{10}H_{16}$. When a smaller quantity of Br is added to a solution of cineol in light petroleum, needles of $(C_{10}H_{18}O)_2Br_2$ are formed (Wallach, *A.* 230, 228). 4. Cineol also combines with *iodine* forming crystals of $(C_{10}H_{18}O)_2I_2$.

Constitution.- Sodium, PCl_5 in the cold, and BzCl at 120° do not act on cineol. Hence it appears not to contain hydroxyl. At 150° BzCl removes H_2O. Hydroxylamine and phenylhydrazine do not act on cineol. Bruhl (*B.* 21, 461) gives cineol the constitution  since it is optically inactive and on passing HCl through it it is converted into optically inactive  .

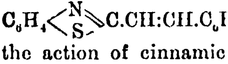
Isomerides of Cineol are described under BORNEOL; *v.* also CAMPHORS, vol. i. p. 672. The matter will be less complicated if we can assume the existence of only two compounds of the formula $C_{10}H_{17}OH$ with rotatory power + 38° and − 38° respectively, the others being mixtures of these in varying proportions. Thus the lævorotatory camphols ($[\alpha]_D$ − 38°) derived from *Blumea balsamifera* (N'gai camphor and also, from the same tree, Bang Phiên), Matico camphor, the camphor from oil of valerian, and that from madder, are in all respects identical (Haller, *C. R.* 103, 64, 151). Ordinary borneol is a cineol of rotatory power + 38°. Camphol from amber appears to be partly of the racemic character (*i.e.* an inactive compound of camphols of rotatory power + 38° and − 38°) and partly of dextrorotatory borneol (Haller, *C. R.* 104, 66). By dissolving a camphol (50 g.) in toluene (150 g.), heating with sodium (6 g.) and passing in cyanogen a product is got whence water extracts a camphyl carbamate $C_{10}H_{17}.O.CO.NH_2$. The product derived from dextrorotatory camphol is described (vol. i. p. 523) as bornyl carbamate. It is dextrorotatory and forms dextro-hemihedral crystals. Lævorotatory camphol forms an isomeride [127°] which is lævorotatory ($[\alpha]_D = -29·90°$), and crystallises in lævo-hemihedral forms. In each preparation, camphyl carbonate $(C_{10}H_{17})_2CO_3$ is a by-product; the carbonate from borneol is dextrorotatory while that from lævorotatory camphol is lævorotatory. Both melt at 215° (Haller, *C. R.* 98, 578).

CINNAMEÏN *v. Benzyl ether* of CINNAMIC ACID.

CINNAMENE *v.* STYRENE.

CINNAMENYL COMPOUNDS $C_6H_5.CH:CH-X$ *v.* STYRYL COMPOUNDS.

CINNAMENYL - AMIDO - PHENYL - MERCAPTAN $C_{15}H_{11}NS$ *i.e.*



$C_6H_4{<}\begin{smallmatrix}N\\S\end{smallmatrix}{>}C.CH:CH.C_6H_5$ [111°]. Prepared by the action of cinnamic acid on amido-phenyl-mercaptan (Hofmann, *B.* 13, 1235). Colourless prisms. Sol. alcohol. Weak base. On fusion with KOH it is split up into cinnamic acid (which is further converted into benzoic acid) and amido-phenyl-mercaptan.

Salts.—B'HCl: unstable salt. $(B'HCl)_2PtCl_4$: yellow needles.

CINNAMIC ACID $C_9H_8O_2$ *i.e.* $C_6H_5.CH:CH.CO_2H$. *Phenyl-acrylic acid. Benzylidene acetic acid.* Mol. w. 148. [133°] (Kraut, *A.* 133, 93; 147, 112). (300°). S.G. $\frac{4}{4}$ 1·248 (Schroder, *B.* 12, 1612). S. ·03 at 17°; S (alcohol) 23 at 20°; S. ($CHCl_3$) 6 at 15°; S. (CS_2) 9 at 15°. *Electrical conductivity*: Ostwald, *J. pr.* [2] 32, 365.

Occurrence.—1. In oil of cinnamon (Dumas a. Péligot, *A. Ch.* 57, 311; Herzog, *Ar. Ph.* 17, 72; 20, 159). 2. In liquid storax which contains styrene, cinnamic acid, and styryl cinnamate (styracin) (E. Simon, *A.* 31, 265; D. Howard, *C. J.* 13, 135; Beilstein a. Kuhlberg, *Z.* [2] 7, 489).—3. In balsam of Peru, which contains benzyl cinnamate, benzoic acid, and cinnamic acid (E. Kopp, *Compt. chim.* 1847, 198; 1849, 116; 1850, 140; Kraut, *B.* 2, 180; Delafontaine, *Z.* 1869, 156).—4. In balsam of Tolu, which is similar in composition to that of Peru (Frémy, *A.* 30, 338; Deville, *A.* 44, 304; E. Kopp, *A.* 60, 269; Busse, *B.* 9, 830).—5. In gum benzoin from Sumatra (Kolbe a. Lautemann, *A.* 119, 136). 6. In the leaves and stalks of *Globularia vulgaris* (Heckel a. Schlagdenhauffen, *A. Ch.* [5] 28, 69). 7. In the leaves of *Enkianthus japonicus* (Eykman, *R. T. C.* 5, 297).

Formation.- 1. By heating benzoic aldehyde with AcCl for 24 hrs. at 125° (Bertagnini, *Cimento*, 4, 46; *A.* 100, 126). 2. By heating benzoic aldehyde with HOAc and $ZnCl_2$ at 160° (Schiff, *B.* 3, 412; *Z.* [2] 6, 700).—3. By heating benzoic aldehyde (2 pts.), Ac_2O (3 pts.), and NaOAc (1 pt.) at 145° (Perkin, *C. J.* 31, 389; Slocum, *A.* 227, 58). This reaction, commonly known as Perkin's synthesis, is discussed under ALDEHYDES (vol. i. p. 108).—4. By the action of benzoic aldehyde on sodium malonate in presence of Ac_2O in the cold, CO_2 being evolved: $Ph.CHO + CH_2(CO_2H)_2 = PhCH:C(CO_2H)_2 + H_2O = PhCH.CH.CO_2H + CO_2 + H_2O$ (Stuart, *C. J.* 43, 404).—5. By heating benzoic aldehyde with malonic acid at 130° (Michael, *Am.* 5, 205).—6. By the action of KOH on benzyl-chloro-malonic ether (Conrad, *B.* 13, 2160).

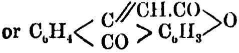
Properties.—Monoclinic prisms (from alcohol) (Schabus, *Sitz. W.* 1850, ii. 206). When quickly distilled it is but little decomposed, but when slowly distilled it splits up into CO_2 and styrene (Howard, *C. J.* 13, 135). Volatile with steam. V. sl. sol. water, v. sol. alcohol, v. e. sol. ether; v. sl. sol. cold ligroin.

Reactions.—1. Distillation with *lime* gives styrene and benzene.—2. *Potash-fusion* gives potassium acetate and benzoate (Chiozza, *A. Ch.* [3] 39, 439; Kraut, *A.* 147, 113). Fusion with NaOH gives CO_2 and benzene (50 p.c. of theoretical) (Barth a. Schreder, *B.* 12, 1257).—3. SO_3 forms sulphobenzoic acid. Boiling with H_2SO_4

diluted with 1 to 1¼ vols. water forms an oil, consisting of distyrene $C_{16}H_{16}$ and distyrenic acid $C_{17}H_{16}O_2$.—4. Conc. HNO_3 gives nitro-benzoic acid, but a more dilute acid gives benzoic aldehyde.—5. Boiling with PbO_2 in aqueous solution forms benzoic aldehyde and lead benzoate (Stenhouse, *A.* 55, 1; 57, 79).—6. *Chromic mixture* also forms benzoic aldehyde (Simon). $KMnO_4$ in feebly alkaline solution acts in the same way (A. Bauer, *A.* 220, 37). $KMnO_4$ in very dilute neutral solution at 0° oxidises cinnamic acid to $PhCH(OH).CH(OH).CO_2H$ (Fittig, *B.* 21, 919). – 7. Br gives di-bromo-phenyl-propionic acid (A. Schmitt, *A.* 127, 319).—8. Fuming HBr gives bromo-phenyl-propionic acid. HI acts in a similar way. –9. *Sodium amalgam* reduces it to phenyl-propionic acid (Erlenmeyer, *A.* 137, 327). Conc. HIAq does the same (Popoff, *Z.* [2] 1, 111). 10. HClO gives chloro-oxy-phenyl-propionic acid (Glaser, *A.* 147, 78; *Z.* [2] 3, 65; 4, 131).– 11. Boiling aqueous K_2SO_3 gives sulpho-phenyl-propionic acid. –12. Chlorine acts on aqueous sodic cinnamate in two ways, viz.:

$$\begin{array}{l}
(1)\ Ph.CH.CH.CO_2Na + Cl_2 \\
= Ph.CHCl.CHCl.CO_2Na \\
= Ph.CH.CHCl.CO.O + NaCl \\
= Ph.CH.CHCl + CO_2 + NaCl \\
(2)\ Ph.CH{:}CH.CO_2Na + Cl_2 + H_2O \\
= Ph.CH{:}CH.CO_2H + HClO + NaCl \\
= Ph.CH(OH).CHCl.CO_2H + NaCl
\end{array}$$

producing ω-chloro-styrene and chloro-oxy-phenyl-propionic acid (Erlenmeyer a. Lipp, *A.* 219, 184). –13. *Diphenylamine* and $ZnCl_2$ at 250° form phenyl-acridine (Bernthsen, *B.* 20, 1552).—14. *m-Oxy-benzoic acid* and H_2SO_4 form a body $C_{16}H_8O_3$ or



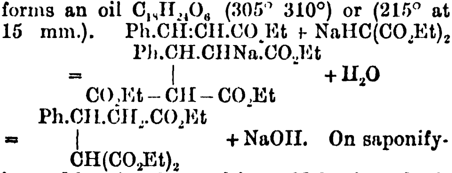
$$C_6H_4\!<\!\begin{array}{c} C /\!\!/ CH.CO \\ CO \end{array}\!>\!C_6H_3\!>\!O$$

[260°] (Kostanecki, *B.* 20, 3137). It forms a diacetyl derivative [260°]. 15. *s-Di-oxy-benzoic acid* and H_2SO_4 give the oxy-derivative of the preceding [325°] which forms a crystalline acetyl derivative $C_{16}H_7AcO_4$ [255°] (K.).– 16. Gallic acid and H_2SO_4 at 50° form, in the same way, 'styrogallol,' a dioxy-derivative of the above $C_{16}H_8O_5$, which crystallises in minute yellow needles, melting above 350° (Jacobsen a. Julius, *B.* 20, 2588). Its di-acetyl derivative melts at 260°.

Salts (Herzog, *J. pr.* 29, 51; E. Kopp, *C. R.* 53, 634).—NH_4A' ½aq: sl. sol. cold water.—KA' ½aq: monoclinic crystals; v. sol. water, m. sol. alcohol.—NaA' ½aq: needles (from dilute NaOHAq).—$NaHA'_2$ (Perkin, *C. J.* 31, 388).—AgA': curdy pp. insol. boiling water.—BaA'_2 aq (Herzog).—BaA'_2 2aq: pearly plates (Kopp).—BaA'_2 3aq: iridescent leaflets or striated prisms (Rebuffat, *G.* 11, 166).—CaA'_2 2aq (H.; R.).—CaA'_2 3aq (K.). S. ·16 at 17°.—SrA'_2 4aq: nacreous needles.—MgA'_2 3aq: white needles.—$CuA'_2(CuO_2H_2)x$: greenish-blue pp.—PbA'_2: crystalline powder or flattened needles.—CdA'_2 2aq.—MnA'_2 2aq.—ZnA'_2 2aq: prismatic needles (from hot water).

Methyl ether MeA'. [34°]. (263° i.V.). S.G. $\frac{36}{0}$ 1·0415. Formed by the action of the ethyl ether on methyl alcohol in presence of NaOMe (Purdie, *C. J.* 51, 628; *cf.* E. Kopp, *C. R.* 21, 1376; Anschütz a. Kinnicutt, *B.* 11, 1220; Weger, *A.* 221, 74). With Br it forms $C_6H_5.CHBr.CHBr.CO_2Me$ [117°].

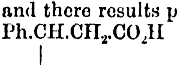
Ethyl ether EtA'. [12°] (Friedländer, *A.* 221, 75). (268°) at 741 mm. (Bruhl, *A.* 235, 19). (271° i. V.)(A. a. K.). S.G. $\frac{20}{4}$ 1·0490. μ_D 1·560 (B.). *Preparation.*– Cinnamic acid (500 g.) is dissolved in dry alcohol (1 litre) and HCl is passed in to saturation. After 3 hrs. the product is poured into ice-cold water. The oil is washed, dissolved in ether, and shaken with aqueous sodic carbonate, dried over $CaCl_2$, and the ether evaporated (Perkin, jun., *C. J.* 45, 172; *cf.* Herzog, *Ar. Ph.* [2] 17, 72; Marchand, *A.* 32, 269; E. Kopp, *J. pr. Pharm.* [3] 11, 72; Plantamour, *A.* 30, 345). *Reactions.*—1. With *bromine* it forms $C_6H_5.CHBr.CHBr.CO_2Et$ [69°].—2. *Sodium-aceto-acetic ether* in presence of alcohol at 100° forms an acid $C_{15}H_{16}O_4$ [140°]. Its silver salt, AgA', forms radiating prisms, insol. water (Michael, *J. pr.* [2] 35, 351).—3. With *sodium malonic ether* at 100° in presence of alcohol it forms an oil $C_{18}H_{24}O_6$ (305°–310°) or (215° at 15 mm.). $Ph.CH{:}CH.CO_2Et + NaHC(CO_2Et)_2$



$$= \begin{array}{c} Ph.CH.CHNa.CO_2Et \\ | \\ CO_2Et-CH-CO_2Et \end{array} + H_2O$$

$$= \begin{array}{l} Ph.CH.CH_2.CO_2Et \\ \ \ | \\ CH(CO_2Et)_2 \end{array} + NaOH.$$

On saponifying and heating the resulting acid CO_2 is evolved, and there results phenyl-glutaric acid



$$\begin{array}{l} Ph.CH.CH_2.CO_2H \\ \ \ | \\ CH.CO_2H \end{array}$$

[138°]. Its silver salt, AgA', is amorphous (Michael, *J. pr.* [2] 35, 349; *Am.* 9, 118).

n-Propyl ether PrA'. (283°–284° i.V.) (A. a. K.). S.G. ^{0} 1·0435 (Weger, *A.* 221, 76).

Benzyl ether $C_6H_5.CH{:}CH.CO\,OCH_2C_6H_5$. *Cinnamein.* [39°]. Discovered by Plantamour (*A.* 27, 329; 30, 341) in balsam of Peru (Frémy, *A. Ch.* 70, 184; E. Kopp, *Compt. chim.* 1850, 140; Schailing, *A.* 74, 230; 97, 184; Kraut, *A.* 107, 208; Grimaux, *Z.* [2] 5, 157). Formed also by boiling dry sodium cinnamate with alcohol and benzyl chloride for some hours. Short prisms (from alcohol).

Phenyl ether $C_6H_5.C_2H_2.CO_2C_6H_5$: [73°]; (206°) at 15 mm. Formed by the action of cinnamoyl chloride upon phenol. By slow distillation it loses carbonic acid, giving stilbene $C_6H_5.C_2H_2.C_6H_5$ (Anschütz, *B.* 18, 1945; *C. J.* 47, 898).

p-Tolyl ether $C_6H_5.C_2H_2.CO_2C_7H_7$: [101°]; (230°) at 15 mm. (A.). By slow distillation it yields *s*-phenyl-tolyl-ethylene (A.).

Phenylpropyl ether $C_6H_5.C_2H_2.CO_2.CH_2.CH_2.CH_2.C_6H_5$. Occurs in storax (Miller, *A.* 189, 353), and is also formed by treating styracin bromide with zinc and H_2SO_4.

Thymyl ether $C_6H_5.C_2H_2.CO_2C_{10}H_{13}$: [70°]; (240°) at 15 mm. (A.).

(β)-*Naphthyl ether* $C_6H_5.C_2H_2.CO_2C_{10}H_7$: [102°]. By distillation CO_2 is split off with formation of *s*-phenyl-naphthyl-ethylene (A.).

Cinnamyl ether $C_6H_5.CH{:}CH.CO.O.CH_2.CH{:}CH.C_6H_5$. *Styracin.* [44°]. S. (ether) 33; S. (alcohol of S.G. ·825) 33 at 78°; 5 at 15°. Occurs in liquid storax (Bonastre, *J. Ph.* 1831, 338; E. Simon, *A.* 31, 265; E. Kopp, *Compt. chim.* 1850, 140; Toel, *A.* 70, 1; Strecker, *A.* 70, 10; 74, 112; Wolff, *A.* 75, 297; Plantamour, *A.* 27, 329; 30, 341; Gossmann, *A.* 99, 376; Scharling, *A.* 97, 90, 174; W. v. Miller, *N. Rep. Pharm.* 24, 1; *A.* 188, 200; 189, 344). Needles or prisms (from alcohol). Chlorine forms a viscid tetra-chloro- derivative $C_{18}H_{12}Cl_4O_2$. Br forms $C_{18}H_{16}Br_2O_2$ [151°] and $C_{18}H_{16}Br_4O_2$.

Chloride $C_6H_5.CH{:}CH.CO.Cl$. [36°]. (170°) at 58 mm. Prisms (Cahours, *A. Ch.* [3] 23, 341; Rostoski, *A.* 178, 214 (Claisen a. Antweiler, *B.* 13, 2123).

Cyanide $C_6H_5.CH{\cdot}CH.CO.CN$. [115°]. Prisms. Sol. ether, $CHCl_3$, C_6H_6, and CS_2; v. sl. sol. water. Prepared from the chloride by the action of silver cyanide. On saponification it gives cinnamoyl-formic acid.

Anhydride $(C_6H_5.CH{:}CH.CO)_2O$. [127°]. (Gerhardt, *A. Ch.* [3] 37, 285; *A.* 87, 76). Crystalline.

Amide $C_6H_5.CH{:}CH.CO.NH_2$. [142°]. (v. Rossum, *Z.* 1866, 362). $(C_6H_5.C_2H_2.CO.NH)_2Hg$.

Anilide $C_6H_5.CH{:}CH.CO.NPhH$ (Cahours, *A.* 70, 43). Slender needles.

Diphenylamide $C_6H_5.CH{:}CH.CO.NPh_2$. [153°] (Bernthsen, *B.* 20, 1554). Needles.

Nitrile $C_6H_5.CH{:}CH.CN$. [11°]. (255°). From the amide and PCl_5. Also from cinnamic acid and lead sulphocyanide at 190° (Krüss, *B.* 17, 1768).

Cinnamic acid dibromide *v.* DI-BROMO-PHENYL-PROPIONIC ACID.

Cinnamic acid hydrobromide *v.* BROMO-PHENYL-PROPIONIC ACID.

Cinnamic-acid-di-nitrite $C_6H_5.C_2H_2(NO_2)_2.CO_2H$. *Phenyl-di-nitro-propionic acid.* Colourless crystals. Formed by direct combination of cinnamic acid with N_2O_4. Very unstable. By treatment with water or alcohol it evolves CO_2 and yields phenyl-nitro-ethylene $C_6H_5.CH{:}CH(NO_2)$ (Gabriel, *B.* 18, 2438).

p-**Aldehydo-cinnamic acid** $C_6H_4(CHO)(CH{:}CH.CO_2H)$. [247°]. From terephthalic aldehyde, NaOAc, and Ac_2O by Perkin's reaction (Low, *A.* 231, 374). Flat prisms or needles. Sl. sol. hot water, ether, or chloroform, more sol. glacial acetic acid. When sublimed it forms large plates. *Salt.*- AgA.

Ethyl ether EtA′. Reduces ammoniacal $AgNO_3$. Gives by Perkin's reaction

$$C_6H_4(CH{:}CH.CO_2H)(CH{:}CH.CO_2Et)$$

(*v.* PHENYLENE-DI-ACRYLIC ACID). *Reactions.* — 1. Reduces ammoniacal $AgNO_3$ with difficulty.— 2. Does not react with NaOAc and Ac_2O.—3. On nitration gives nitro-aldehydo-cinnamic acid (*q. v.*).

Di-bromide $C_6H_4(CHO).CHBr.CHBr.CO_2H$. [176°] (with decomposition). Prisms (from methyl alcohol). Insol. water; v. sol. ether, chloroform, and alcohol.

p-**Carboxy-cinnamic acid** $C_6H_4(CO_2H)(CH{:}CH.CO_2H)$ [1:4]. Got by saponifying its ether. Powder, will not melt, but may be sublimed. Nearly insoluble in solvents. Does not combine with bromine in the cold. Forms a nitro- derivative.

Dibromide $C_6H_4(CO_2H)(CHBr.CHBr.CO_2H)$. *Di-bromo-carboxy-phenyl propionic acid.* Formed at 100° Will not melt. Sol. methyl alcohol, from which it may be crystallised.

Mono-ethyl ether $C_6H_4(CO_2Et)(CH{:}CH.CO_2H)$ [220°]. From *p*-aldehydo-terephthalic ether, NaOAc, and Ac_2O by Perkin's reaction (Löw, *A.* 231, 369). Prisms (from ether).

Other derivatives of cinnamic acid are described as AMIDO-, BROMO-, CHLORO-, HYDRAZIDO-, NITRO-, SULPHIDO-, SULPHYDRO-, and SULPHO-CINNAMIC ACID. Oxy-cinnamic acid is described as COUMARIC ACID.

CINNAMIC ALDEHYDE C_9H_8O *i.e.* $C_6H_5.C_2H_2.CHO$. Mol. w. 132. (129°). S.G. $\frac{20}{4}$ 1·0497 (Brühl, *A.* 235, 18). $\mu_D = 1{\cdot}619$. $\mu_\gamma = 1{\cdot}683$.

Occurrence.—In oil of cassia and oil of cinnamon, whence it may be extracted by shaking with $NaHSO_3$ and distilling the resulting crystalline compound with aqueous Na_2CO_3 (Perkin, *C. J.* 31, 403; *cf.* Mulder, *A.* 34, 147; Bertagnini, *A.* 85, 271).

Formation.—1. By oxidising cinnamyl alcohol with the aid of platinum black (Strecker, *A.* 93, 370).—2. By distilling calcium formate with calcium cinnamate (Piria, *A.* 100, 105).

Preparation.—A mixture of benzoic aldehyde (10 pts.), acetic aldehyde (15 pts.), 10 pts. of 10 p.c. aqueous NaOH, and 900 pts. of water is allowed to stand for 8 or 10 days with frequent shaking at about 30°, the cinnamic aldehyde being finally extracted with ether (Chiozza, *A.* 97, 350; Peine, *B.* 17, 2109).

Properties.—Oil. Forms crystalline compounds with HCl, HNO_3, $NaHSO_3$, $KHSO_3$, and NH_4HSO_3 (Dumas a. Péligot, *A.* 14, 65).

Reactions.— With alcoholic NH_3 it gives hydrocinnamide $C_{27}H_{24}N_2$ [106°]. With HCN it yields the nitrile of *a*-oxy-phenyl-crotonic acid. With resorcin and dilute HCl it gives a resin in the cold (Michael a. Ryder, *Am.* 9, 134). HCl passed into a mixture of cinnamic aldehyde with phenyl mercaptan forms $C_6H_5C_2H_2CH(SPh)_2$ [81°] (Baumann, *B.* 18, 885). With carbamic ether it forms $Ph.C_2H_2.CH(NH.CO_2Et)_2$ [135°–143°] (Bischoff, *B.* 7, 1079).

Phenyl hydrazide $C_6H_5.C_2H_2.CH{:}N_2HC_6H_5$: [168°], yellow plates (Fischer, *B.* 17, 575).

Anilide $C_6H_5.C_2H_2.CH{:}NC_6H_5$: [109°], yellow glistening plates. Very stable towards HCl. Forms crystallisable salts with acids (Doebner a. Miller, *B.* 16, 1665; Peine, *B.* 17, 2109).

Di-methyl-amido-anilide $C_6H_5.C_2H_2.CH{:}N.C_6H_4(NMe_2)$: [141°]; yellow needles; sol. alcohol, sl. sol. cold ether (Nuth, *B.* 18, 574).

Ethylene-di-amide $(C_6H_5.C_2H_2.CH{:}N)_2C_2H_4$: [110°]; tables, m. sol. ether (Mason, *B.* 20, 267).

Di-bromide *v.* *aβ*-DI-BROMO-PHENYL-PROPIONIC ALDEHYDE.

CINNAMIC ALDOXIM $C_6H_5.CH{:}CH.CH{:}NOH$. *Phenyl-acrylic aldoxim.* [136°]. Fine silky needles. V. sol. alcohol, ether, acids, and alkalis, nearly insol. cold water and ligroïn.

Benzoyl derivative $C_6H_5.C_2H_2.CH{:}NOBz$. [125°]. White needles; sl. sol. cold alcohol and benzene, insol. water and ligroïn (Bornemann, *B.* 19, 1512).

CINNAMIC-CARBOXYLIC ACID *v. Carboxy-*cinnamic acid.

CINNAMIDOXIM $C_9H_{10}N_2O$ *i.e.* $C_6H_5.CH:CH.C(NOH)NH_2$. *Phenyl-allenyl-amidoxim.* [93°]. Formed by direct combination of cinnamo-nitrile with hydroxylamine. Rod-like prisms. Sol. hot, less sol. cold water, v. sol. alcohol, ether, and benzene, sl. sol. ligroin. Decomposed by long boiling with water.

Salts.— B'HCl: [155°], flat concentric prisms.— $B'_2H_2Cl_2PtCl_4$: concentric needles, sol. alcohol.

Methyl ether $C_8H_7.C(NH_2)NOMe$: [98°]; prisms; volatile with steam; v. sol. alcohol, ether, &c., nearly insol. cold water, more readily in hot.

Ethyl ether $C_8H_7.C(NH_2)NOEt$: [83°]; like the preceding.

Benzoyl derivative $C_8H_7.C(NH_2)NOBz$: [160°]; fine needles; v. sol. alcohol, more sparingly sol. benzene, chloroform, and ether, insol. cold water. On boiling with water it loses 1 mol. H_2O, giving phenyl-allenyl-azoxim-benzenyl (Wolff, *B.* 19, 1507).

CINNAMO-LACTONE *v.* Coumarin.

CINNAMONE *v.* Di-benzylidene-acetone.

CINNAMOYL-ACETO-ACETIC ETHER $C_{15}H_{16}O_4$ *i.e.* $Ph.CH:CH.CO.CHAc.CO_2Et$. [40°]. From sodium aceto-acetic ether and cinnamoyl chloride (Fischer a. Kuzel, *B.* 16, 166). Crystalline grains (from ligroin).

a-**CINNAMOYL-BUTYRIC ETHER** *v. Benzylidene-ethyl-*aceto-acetic ether, vol. i. p. 24.

CINNAMOYL-FORMIC ACID *v.* Styryl-glyoxylic acid.

CINNAMYL ALCOHOL $C_9H_{10}O$ *i.e.* $C_6H_5.CH:CH.CH_2OH$. *Styrone.* Mol. w. 134. [33°]. (254°) at 747 mm. S.G. $\frac{20}{4}$ 1·0140. μ_D 1·582 at 20° (Brühl, *A.* 235, 16). R_∞ 69·7 (in a 9 p.c. alcoholic solution) (Kanonnikoff; Nasini a. Bernheimer, *G.* 14, 153). Obtained by distilling styracin (cinnamyl cinnamate) with aqueous potash (Simon, *A.* 31, 274; Ramdohr, *Z. Pharm.* 1858, 113; *J.* 1858, 446; Tol, *A.* 70, 3). Long thin needles, smelling like hyacinths. Sl. sol. cold water, v. e. sol. alcohol and ether.

Reactions.—1. *Oxidised* by air and platinum black to cinnamic aldehyde; and by chromic acid mixture to cinnamic acid and benzoic aldehyde.—2. Boiling with aqueous KOH and PbO_2 gives benzoic aldehyde.—3. Reduced by *sodium amalgam* in presence of much water to phenyl-propyl alcohol (Rügheimer, *A.* 172, 122). Reduced by (15 p.c.) sodium amalgam by heating with a little water for 3 days at 100° it forms styrene C_8H_8 and methyl alcohol, as follows:

$$PhCH:CH.CH_2OH + H_2 = Ph.CH:CH_2 + CH_3OH$$

(Hatton a. Hodgkinson, *C. J.* 39, 319).—4. Aqueous HI (S.G. 1·96) at 190° gives toluene and allyl-benzene (Tiemann, *B.* 11, 671).—5. Fuming H_2SO_4 forms $C_9H_{11}SO_3H$ (?) (Jacobsen, *A.* 146, 90).—6. B_2O_3 forms cinnamyl oxide $(C_9H_9)_2O$, a heavy oil.

Acetyl derivative C_9H_9OAc. (245°).

CINNAMYLAMINE $C_9H_{11}N$ *i.e.* $C_6H_5.CH:CH.CH_2.NH_2$. (100°). From cinnamyl chloride and alcoholic NH_3 at 100° (Ramdohr, *Z. Pharm.* 1858, 113; *J.* 1858, 448). According to Malbot (*C. R.* 105, 574) the chief product is di-cinnamyl-amine.—B'HCl: stellate groups of crystals.—$B'_2H_2PtCl_6$: sl. sol. cold water.

CINNAMYL CHLORIDE C_9H_9Cl *i.e.* $C_6H_5.CH:CH.CH_2Cl$. A liquid, obtained by passing HCl into cinnamyl alcohol. NaOEt converts it into oily C_9H_9OEt (Ramdohr, *Z. Pharm.* 1858, 113; *J.* 1858, 448). K_2S forms oily $(C_9H_9)_2S$.

CINNAMYLIDENE - DIACETONAMINE *v.* vol. i. p. 28.

CINNAMYLIDENE - DI - THIO - GLYCOLLIC ACID $Ph.CH:CH.CH:(SCH_2CO_2H)_2$. [143°]. Formed by the action of cinnamic aldehyde on thio-glycollic acid (Bongartz, *B.* 21, 481). White plates (from hot water). By the action of zinc-dust in an alkaline solution cinnamyl thio-glycollic acid is formed.

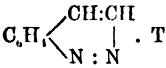
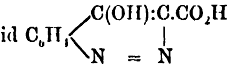
CINNAMYL IODIDE C_9H_9I. From cinnamyl alcohol and PI_3. Oil. Converted by alcoholic KCy into oily C_9H_9Cy.

DI-CINNAMYL KETONE *v.* Di-benzylidene-acetone.

CINNAMYL-METHYL KETONE *v.* Benzylidene acetone.

CINNAMYL-PHENYL-KETONE *v.* Phenyl-cinnamyl-ketone.

CINNAMYL-THIO-GLYCOLLIC ACID $Ph.CH:CH.CH_2.S.CH_2.CO_2H$. [77°]. The compound obtained by the action of cinnamic aldehyde on thioglycollic acid when treated with zinc-dust in an alkaline solution yields this substance (Bongartz, *B.* 21, 481). White plates (from dilute alcohol).

CINNOLINE $C_8H_6N_2$ *i.e.*  $C_6H_4\left\langle\begin{array}{l}CH:CH\\ \qquad\ |\\ N\ :\ N\end{array}\right.$. This base has not been isolated. The first of its derivatives prepared was oxy-cinnoline carboxylic acid  $C_6H_4\left\langle\begin{array}{l}C(OH):C.CO_2H\\ \qquad\quad |\\ N\ =\ N\end{array}\right.$ obtained by warming *o*-diazo-phenyl-propiolic acid with water (Richter, *B.* 16, 677; *v.* also Widman, *B.* 17, 722).

CINNYL. A name sometimes applied to the radicle cinnamyl $Ph.CH:CH.CH_2$.

CIRCULAR POLARISATION *v.* Physical methods.

CITRACETIC ACID $C_6H_6O_6$. An acid said to be formed, together with aceconitic acid, by treating bromo-acetic ether with sodium (Baeyer, *A.* 135, 306).—$Ba_3A'''_2$2aq: gummy. —$Pb_3A'''_2$ 2aq.

CITRA-DI-BROMO-PYROTARTARIC ACID *v.* Di-bromo-pyrotartaric acid.

CITRA - CHLORO - PYROTARTARIC ACID *v.* Chloro-pyrotartaric acid.

CITRACONANIL *v. Phenylimide of* Citraconic acid.

CITRACONIC ACID $C_5H_6O_4$. Mol. w. 130. [80°]. S.G. 1·6. S. 238. R_∞ 41·68 (in a 7 p.c. aqueous solution) (Kanonnikoff, *J. pr.* [2] 32, 497). H.C. 477867 (Louguinine, *C. R.* 106, 1291). *Heat of solution*: 2793 (Gal a. Werner, *Bl.* [2] 47, 159). *Heat of neutralisation*: 27082 (G. a. W.).

Formation.—1. The anhydride is the chief portion of the distillate obtained by heating citric acid. It rapidly combines with water (Lassaigne, *A. Ch.* [2] 21, 100; Robiquet, *A. Ch.* 75, 78; Liebig, *A.* 26, 119, 152; Gottlieb, *A.* 77, 265; Baup, *A. Ch.* [3] 33, 192; Kämmerer, *A.* 170, 191; Wilm, *A.* 141, 28).—2. By the distillation of itaconic acid (Crasso, *A.* 34, 68), of lactic acid (Engelhardt, *A.* 70, 246), of citramalic acid (Carius, *A.* 129, 160), and of oxypyrotartaric acid (Demarçay, *C. R.* 82, 1337).

Properties.—Monoclinic four-sided prisms. Deliquescent. V. sol. water, alcohol, and ether. Volatile with steam. By dry distillation it is partially resolved into its anhydride.

Reactions. – 1. *Sodium amalgam* in presence of water reduces it to pyrotartaric acid. 2. *Bromine* unites with it in the cold, forming citra-di-bromo-pyrotartaric acid (Kekulé, *J.* 1862, 313).—3. Fuming *hydric bromide* unites with it even in the cold, forming citra-bromo-pyrotartaric acid. —4. *Electrolysis* of the potassium salt forms allylene $CH_3.C:CH$.—5. *Water* at 120° changes it to the isomeric itaconic acid.—6. Boiling dilute HNO_3 forms mesaconic acid.—7. *Chlorine* acting on sodium citraconate in aqueous solution forms chloro-citramalic, chloro-methacrylic, and tri chloro-isobutyric acids and tri-chloro-acetone (Gottlieb, *J. pr.* [2] 12, 1; Morawski, *J. pr.* [2] 12, 369).

Salts.—NH_4HA''.—CaA''aq. $CaH_2A''_2$ 3aq. CaA'' 5aq (Kämmerer, *A.* 148, 326). — $SrH_2A''_2$ 3aq. $BaH_2A''_2$ aq: silky needles. — BaA'' $2\frac{1}{3}$aq (Kämmerer, *A.* 170, 191; Petri, *B.* 14, 1631). — $PbH_2A''_2$. — PbA''. — PbA'' 2aq. — $PbA''PbO$.—$AgHA''$.—Ag_2A''.—Ag_2A'' aq: hexagonal crystals.

The acid aniline salt $HA''NH_3Ph$ loses H_2O when its aqueous solution is allowed to stand for a few days, and deposits crystals of the acid anilide $CO_2H.C_3H_4.CO.NPhH$.

The neutral aniline salt when boiled with water gives the phenyl-imide $C_3H_4(C_2O_2)NPh$.

The ethyl-aniline and methyl-aniline salts do not give anilides when heated. The same is the case with $C_6H_5.NMe_2$ and $C_6H_5.NEt_2$ salts.

The ethyl derivatives of *p*-toluidine behave exactly like the corresponding aniline compounds.

Di-phenyl-amine citraconate is only formed at 100°, since the Ph_2NH separates completely on cooling (Michael, *Am.* 9, 194).

Methyl ether Me_2A''. (212° i. V.). S. 3 at 15°. S.G. $\frac{15}{15}$ 1·1168; $\frac{30}{30}$ 1·1050. μ_D 1·4442; μ_H 1·4721 at 15·5°. From citraconic acid, methyl alcohol, and HCl (Perkin, *C. J.* 39, 555). From silver citraconate and MeI. Oil; pleasant odour.

Ethyl ether Et_2A''. (232° i. V.). S.G. $\frac{15}{15}$ 1·051; $\frac{30}{30}$ 1·038. M.M. 10·499 (Perkin, *C. J. Proc.* 3, 99). μ_D 1·4397; μ_H 1·4659 at 16·5° (Gladstone). An alcoholic solution with sodium-aceto-acetic ether at 100° forms an oil $C_{15}H_{24}O_7$ (174°) at 26 mm. (Michael, *J. pr.* [2] 35, 354; *Am.* 9, 118).

Chloride $C_3H_4(COCl)_2$. (95°) at 17·5 mm. S.G. $^{16\cdot 4}$ 1·408. From the acid and PCl_5 (Strecker, *B.* 15, 1640).

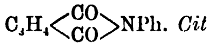
Anhydride $C_3H_4C_2O_3$. [7°]. (214° i. V.). S.G. $\frac{14}{4}$ 1·241 (Anschutz, *B.* 13, 1542; 14, 2788). Partially converted by distillation into xeronic anhydride (Fittig, *A.* 188, 64). Thiourea at 130° converts it into $NH_2.CS.NH.CO.C_3H_4.CO_2H$ [223°] (Pike, *B.* 6, 1106).

Amide $C_5H_4O_2(NH_2)_2$. Thin colourless tables, sol. water, decomposes at about 186° (Strecker, *B.* 15, 1640).

Imide $C_5H_4O_2(NH)$. [110°]. Formed by distilling acid ammonium citraconate (Gottlieb, *A.* 77, 274; Ciamician a. Dennstedt, *G.* 12, 501). Needles (from water). Br forms $C_5H_3BrO_2(NH)$ [c.181°] and $C_5H_2Br_2O_2(NH)$ [c.144°]. $C_5H_4O_2NAg$ (Mendini, *G.* 15, 184).

Anilide $C_5H_4O_2(NHPh)_2$: [176°], long flat needles, sol. alcohol and ether, slightly in water (Strecker, *B.* 15, 1639).

Acid anilide $CO_2H.C_3H_4.CO.NHPh$. *Citraconanilic acid.* Formed spontaneously by allowing the aqueous solution of the acid aniline salt to stand for a few days. Large trimetric prisms or long needles.



Phenylimide $C_3H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>NPh$. *Citraconanil*: [98°], formed by boiling aniline and citraconic acid in aqueous solution (Michael a. Palmer, *B.* 19, 1375; *Am.* 9, 180).

p-Chloro-phenylimide $C_3H_4:C_2O_2:NC_6H_4Cl$. [114°]. From the preceding and Cl (Morawski a. Klaudy, *M.* 8, 399).

Bromo-phenylimide ×$C_3H_4O_2.N.C_6H_4Br$, [118°]. From the phenylimide and Br (M. a. K.).

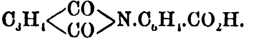
Di-nitro-phenylimide $C_3H_4:C_2O_2:N.C_6H_3(NO_2)_2$. [120°]. From the preceding, HNO_3 and H_2SO_4 (Gottlieb, *A.* 85, 21).

Acid toluide ×$CO_2H.C_3H_4.CO.NHC_7H_7$ [166°]. Formed by warming an aqueous solution of acid *p*-toluidine citraconate.

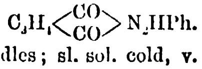
p-Tolylimide $C_3H_4:C_2O_2:NC_6H_4Me$. [115°].

(α)-*Naphthylimide* $C_5H_4O_2NC_{10}H_7$. [142°]. (360°). Yellow plates, sol. most solvents, insol. conc. HClAq (Morawski a. Gläser, *M.* 9, 286).

(β)-*Naphthylimide* $C_{15}H_{11}O_2N$. [110°]. From citraconic acid and (β)-naphthylamine at 175° (M. a. G.). Pale yellow needles.



m-Carboxy-phenylimide $C_3H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>N.C_6H_4.CO_2H$. [218°]. Formed by boiling *m*-amido-benzoic acid with an aqueous solution of citraconic acid. Prismatic needles, sol. hot alcohol and water, sol. dilute alkalis.



Phenyl-hydrazide $C_3H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>N_2HPh$. [160°]. Bright yellow needles; sl. sol. cold, v. sol. hot, water.

Isomerides of Citraconic Acid *v.* Itaconic acid, Mesaconic acid, Crotaconic acid, and Ethylidene-malonic acid.

Constitution of Citraconic acid.—Citraconic acid stands to mesaconic acid in the same relation that maleic acid does to fumaric acid. The formation of allylene by the electrolysis of citraconic and mesaconic acids indicates the presence of a methyl group, so that citraconic acid is methyl-maleic acid, while mesaconic acid is methyl-fumaric acid. On the other hand, itaconic acid is said to give isoallylene $CH_2:C:CH_2$ on electrolysis.

Citraconic and maleic acids differ from the *allo*-isomerides in combining vigorously with halogens and HBr. The ethers of citraconic and maleic acids have higher boiling-points than those of mesaconic and fumaric acids, the difference being much greater between the methyl than the ethyl ethers.

On the other hand, (α)-coumaric ethers have *lower* boiling-points than (β)-coumaric ethers.

Citraconic acid with PCl_5 gives mesaconyl chloride, (α)-coumaric acid with PCl_5 gives (β)-coumaryl chloride (Petri, *B.* 14, 1634).

The indices of refraction of the citraconic and mesaconic ethers are nearly the same for the red end of the spectrum, but the mesaconic ethers refract the violet rays more powerfully.

The ethers of citraconic, maleic, and (α)-coumaric acids contract in volume on changing to the more stable isomerides. The acid aniline salts of citraconic and maleic acids readily change, especially when their solution is evaporated at 100°, into phenylimides; the corresponding salts of mesaconic and fumaric acids are not affected (Perkin, *C. J.* 39, 561).

The initial velocity of etherification is 29·3 for itaconic acid, 37·9 for mesaconic acid, and 47·4 for citraconic acid (Menschutkin, *J. R.* 13, 527; *B.* 14, 2630).

CITRAMALIC ACID *v.* OXY-PYROTARTARIC ACID.

CITRANILIC ACID *v. Phenylimide of* CITRIC ACID.

CITRATARTARIC ACID *v.* DI-OXY-PYROTARTARIC ACID.

CITRAZIC ACID *v.* DI-OXY-PYRIDINE-CARBOXYLIC ACID.

CITRENE *v.* TERPENES.

CITRIC ACID $C_6H_8O_7$ *i.e.* $CO_2H.CH_2.C(OH)(CO_2H).CH_2.CO_2H$. [147°] (Grimaux a. Adam). S.G. 1·54. S. 125 at 15°; 200 at 100°. S. (of $C_6H_8O_7$ aq in 80 p.c. alcohol) 87 at 15°; S. (of $C_6H_8O_7$ in absolute alcohol) 75·9 at 15°; S. (of $C_6H_8O_7$ in ether) 2·26 (Bourgoin, *Bl.* [2] 29, 244); S. (of $C_6H_8O_7$ in ether) 9·1 (Lippmann, *B.* 12, 1650). H.F. 354,000 (v. Rechenberg).

Occurrence. In lemons, oranges, cranberries, cowberries, and sundew (*Drosera intermedia*); together with malic acid in red currants, gooseberries, whortleberries, raspberries, and cloudberries (*Rubus Chamæmorus*); together with both malic and tartaric acids in tamarinds and mountain ash berries (Scheele, *Opuscula*, 2, 181; Berzelius, *A. Ch.* 94, 171; [2] 52, 424, 432; 67, 303; 70, 215; Robiquet, *A. Ch.* [2] 65, 68; Liebig, *A.* 5, 134; 26, 119, 152; 44, 57; Marchand, *J. pr.* 23, 60; Cahours, *A. Ch.* [3] 19, 488; Pebal, *A.* 82, 78; 98, 67; Tilley, *J. Ph.* 13, 305; Perret, *Bl.* [2] 5, 42; Warrington, *C. J.* 28, 925; Stein, *B.* 12, 1603; Kossovic, *C. C.* 1887, 1157). Occurs also in certain plants, *e.g.* celandine (Haitinger, *M.* 2, 485), leaves of the wild cherry (Rochleder, *Z.* [2] 6, 176), *Lupinus luteus*, *Vicia sativa* (vetch), *Vicia Faba*, *Pisum sativum* (peas) and white beans (*Phaseolus*) (Ritthausen, *J. pr.* [2] 29, 357). Occurs as lime and potash salt in tobacco, and in the juice of lettuce. Occurs in the root and leaves of madder (Rochleder, *A.* 80, 322; Willigk, *A.* 82, 343), in beetroot (Michaelis, *J.* 1851, 394; *J. pr.* 54, 184; Schrader, *A.* 121, 370), and in young vines (Wittstein, *J.* 1857, 520; *Vier. pr. Pharm.* 6, 192).

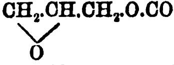
Synthesis.—*s*-Di-chloro-acetone combines with hydrogen cyanide forming $(CH_2Cl)_2C(OH).CN$ which is converted by saponification into $(CH_2Cl)_2C(OH).CO_2H$, whence KCy readily forms $(CN.CH_2)_2C(OH).CO_2H$ which is converted by treatment with HCl into citric acid (Grimaux a. Adam, *A. Ch.* [5] 23, 356; *C. R.* 90, 1252).

Preparation.—Lemon juice is allowed to undergo incipient fermentation, and is then boiled with chalk and lime. The ppd. calcium citrate is decomposed by an equivalent quantity of H_2SO_4.

Properties.—Usually crystallises in efflorescent trimetric prisms (containing aq) $a:b:c$ = ·6068:1:·4106. Different specimens of crystallised citric acid when powdered and left over H_2SO_4 lose water at very different rates (Grosjean, *C. J.* 43, 331). From boiling solutions citric acid separates in anhydrous crystals (Sarandinaki, *B.* 5, 1101). Crystals containing 2aq may sometimes be obtained (Cloez). Lime water produces little or no pp. in the cold, but calcium citrate is ppd. on boiling. Calcium citrate is insoluble in KOH; it dissolves in NH_4Cl, but is reppd. on boiling. Citric acid differs also from tartaric acid in not forming an insoluble acid potassium salt. Boiling, strongly alkaline, permanganate is reduced by citric acid to manganate only, the liquid becoming green, whereas in the case of tartaric acid the reduction proceeds further, the liquid becoming brown (Chapman a. Smith, *Laboratory*, 1, 39; *cf.* Wimmel, *Z.* [2] 5, 286). $FeCl_3$ gives a light yellow pp. in a hot solution of an alkaline citrate; the pp. dissolves in excess of the citrate (Kammerer, *Fr.* 8, 298). Silver citrate dissolves in hot water without blackening. Conc. $K_2Cr_2O_7Aq$ is blackened in the cold by tartaric acid but not by citric acid.

Estimation (in lemon juice).—The juice is neutralised with Na_2CO_3, $CaCl_2$ is added, and the liquid boiled. The pp. is collected and washed. The filtrate and washings are treated with NH_3 and evaporated to a small bulk. Some more calcic citrate then separates (Grosjean, *C. J.* 43, 332; *cf.* Fleischer, *Ar. Ph.* [3] 5, 97; Allen, *C. N.* 32, 277; Creuse, *Ph.* [3] 2, 547). A second concentration may then be effected, when a third quantity sometimes separates. Turmeric is better than litmus as an indicator in alkalimetric experiments with citric acid (F. Watts, *S. C. I.* 5, 214).

Reactions.—1. By *heat* it is split up at 175° into H_2O and aconitic acid $C_6H_6O_6$, which on dry distillation again splits up into CO_2, itaconic acid $C_5H_6O_4$, citraconic anhydride $C_5H_4O_3$, and acetone.—2. By heating with *water* (10 pts.) at 160° it is split up into itaconic acid and CO_2 (Markownikoff a. Purgold, *Z.* [2] 3, 264).—3. Citric acid (100 g.) heated with *water* (50 g.) and sulphuric acid (100 g.) for 5 hours gives aconitic acid which separates on cooling (Hentschel, *J. pr.* [2] 35, 206). 100 g. citric acid heated with 100 g. water and 5 g. H_2SO_4 at 170° give aconitic and itaconic acids (Pawolleck, *A.* 178, 152).—4. Conc. H_2SO_4 at 40° gives off CO, CO_2, and acetone, and forms an acid whose acid barium salt is $(C_5H_7SO_6)_2Ba$, and is converted by baryta-water into $(C_4H_5SO_4)_2Ba$ (Wilde, *A.* 127, 170).—5. On dry distillation with glycerin, it gives, besides acetone, acrolein, CO, and CO_2, a distillate containing the pyruvic ether of glycide



$CH_2.CH.CH_2.O.CO.CO.CH_3$. [82°]. (211°)

(De Clermont a. Chautard, *C. R.* 105, 520).—6. Conc. HClAq at 150° gives aconitic acid; at 200° it also forms diconic acid $C_9H_{10}O_6$, and gives off CO and CO_2 (Hergt, *J. pr.* [2] 8, 373).—7. An aqueous solution mixed with yeast and chalk and exposed to the air at 25° forms acetic and butyric acids (How, *C. J.* 5, 1; Personne, *C. R.* 36, 197). 8. *Chlorine* acting on a conc. aqueous solution of sodium citrate forms hexa-chloro-acetone and chloroform. Br acts in the same way (Cloez, *C. R.* 53, 1120).—9. *Potash-fusion* gives oxalic and acetic acids (Liebig, *A.* 26, 158). 10. Acetone is formed by distilling sodium citrate with lime (Freidl, *M.* 4, 151).—11. Anhydrous citric acid is converted by a mixture of fuming HNO_3 (1 pt.) and H_2SO_4 (2 pts.) into the **nitrate** $C_3H_4(ONO_2)(CO_2H)_3$ erroneously called nitro-citric acid. It is insol. ether, and forms insoluble salts $Ba_3A'''_2$ and $Pb_3A'''_2$ (Champion a. Pellet, *Bl.* [2] 24, 448).—12. Citric acid (1 mol.) heated with *glycerin* (1 mol.) at 100° forms glyceryl citrate $C_3H_5.C_6H_5O_7$ a glassy mass, insol. water (Bemmelen, *J. pr.* 69, 84). Excess of glycerin at 170° gives so-called **citro-diglycerin** $C_{12}H_{18}O_{10}$(?).—13. Citric acid (1 mol.) heated with *mannite* (1 mol.) at 140° forms **citromannitan** $C_{12}H_{14}O_9$ (Bemmelen, *J.* 1858, 435). Excess of citric acid (2 mols.) heated with mannite at 150° forms **dicitromannitan** $C_{18}H_{20}O_{15}$. Both bodies are amorphous.

Salts.—NH_4H_2A''': triclinic crystals.—$(NH_4)_2HA''$. S.G. $^{22}_{4}$ 1·479 (Clarke, *Am.* 2, 174).—$(NH_4)_3A'''$aq: deliquescent. Ferric and aluminium oxides, freshly precipitated, dissolve in a solution of ammonium citrate, and from the solutions when evaporated salts of the general type $C_6H_5O_7H(NH_4)_2(C_6H_5O_7(NH_4)_2)_3M2H_2O$ crystallise out. Similarly magnesium, manganese, nickel, cobalt, zinc, copper, and mercuric oxides dissolve in ammonium citrate to form salts of general type $[C_6H_5O_7(NH_4)_2]_2M$ generally with 1 mol. H_2O. Solutions of these salts are not precipitated by ammonia, the alkaline hydroxides and carbonates, but completely precipitated by H_2S or ammonium sulphide. The oxides and carbonates of Ba, Sr, and Ca decompose boiling solutions of ammonium citrate forming insoluble pps. of the corresponding salts $Ca_3A'''_2$, &c. (Landrin, *A. Ch.* [5] 25, 233; *C. R.* 86, 1336).—$(NH_4)_3H_3A'''_2$ (Heusser, *P.* 88, 121).—Li_3A''' (?) (Thomson, *Ph.* [3] 13, 783).—NaH_2A''' aq.—Na_2HA''' aq: needles.—$Na_3A'''\,5\frac{1}{2}$aq. S.G. $\frac{23\cdot8}{4}$ 1·858 (Clarke, *Am.* 2, 174; Kämmerer, *A.* 148, 294; 170, 176). Trimetric prisms or groups of silky needles.—Na_3A''' 2aq (Heldt, *A.* 47, 157).—KH_2A''' 2aq.—K_2HA'''.—K_3A''' aq.—$K_3(NH_4)_2HA'''_2$.—$K_2(NH_4)A'''$.—$K_3Na_3A'''_2\,6\frac{1}{2}$aq. $K_3Na_3A'''_2$ 11aq.—Tl_3A''' (Kuhlmann, *C. R.* 55, 607).—$Ba_3A'''_2$ 7aq: amorphous pp.—$Ba_3A'''_2$ 5aq: groups of minute needles, formed by boiling the above with water.—$Ba_3A'''_2\,3\frac{1}{2}$aq: minute monoclinic prisms, formed by treating either of the two preceding salts with ammonia.—$Sr_3A'''_2$ 5aq: minute silky needles.—$Sr_3A'''_2$ 2aq. $Sr_7H_2(C_6H_4O_7)_4$ 11aq.—$Sr_7H_2(C_6H_4O_7)_4\,2\frac{1}{2}$aq.—$Ca_3A'''_2$ 4aq. From Na_3A''' and $CaCl_2$: pp. changed in water at 100° into minute transparent needles. $Ca_3A'''_2$ 7aq.—$CaH_2A'''_2$ aq.—$Mg_5H_2(C_6H_4O_7)_3$ 8aq. $Mg_3A'''_2$ 9aq.—$Mg_3A'''_2\,5\frac{1}{2}$aq.—$Mg_3A'''_2$ 7aq.—$Mg_{11}H_2(C_6H_4O_7)_6$ 13aq.—$Mg_8H_4(C_6H_4O_7)_5$ 3aq.—$Mg_3A'''_2$ 14aq.—$Mg(NH_4)_4A'''_2$ 2aq (Landrin, *C. R.* 86, 1336).—$Zn_3A'''_2$ 2aq.—$Zn_8H_4(C_6H_4O_7)_5$.—$Zn_5H_2A'''_4$ 2aq.—$Zn(NH_4)_4A'''_2$.—$Cd_3A'''_2\,\frac{1}{2}$aq.—$Cd_3A'''_2$ 10aq.—$Cd_9H_2(C_6H_4O_7)_5$ 18aq: needles.—$Cd_9H_2(C_6H_4O_7)_5$ 27aq.—$Cu_2C_6H_4O_7\,2\frac{1}{2}$aq: green crystalline precipitate which is obtained by boiling a solution of cupric carbonate in citric acid.—$Cu_5H_2(C_6H_4O_7)_3$ 15aq: greenish pp. got by adding alcohol to the above solution.—$Cu(NH_4)_4A'''_2$ aq (Landrin, *C. R.* 86, 1336).—$Pb_3A'''_2$ 3aq: crystalline pp. from lead nitrate and Na_3A'''.—$Pb_2C_6H_4O_7$ 2aq: amorphous; got by heating the preceding with ammonia.—$Pb_3A'''_2$ aq: amorphous pp. from alcoholic $Pb(OAc)_2$ and citric acid.—$PbHA'''$: crystals, v. sol. water.—$Pb_3A'''_2Pb_2O_2$ 3aq (at 100°) (Otto, *A.* 127, 175).—$Pb_3A'''_2Pb_4O_4$.—$Hg(NH_4)_4A'''_2$.—$Co_3A'''_2$ 14aq: amorphous.—$Co(NH_4)_4A'''_2$ 4aq.—$Ni_3A'''_2$ 14aq: amorphous.—$Ni(NH_4)_4A'''_2$ 4aq.—$Mn_3A'''_2$ 2aq: crystalline powder formed by boiling citric acid with $MnCO_3$ (Heldt); the following salts are formed at the same time (K.). Sodium citrate does not precipitate salts of manganese.—$MnHA'''$ aq.—$Mn_3A'''_2$ 9aq: trimetric prisms.—$Mn_5H_2(C_6H_4O_7)_3$ 15aq.—$Mn_7H_2(C_6H_4O_7)_4$ 18aq.—$Mn(NH_4)_4A'''_2$.—$FeHA'''$aq: crystalline powder formed by boiling iron with aqueous citric acid.—$FeNaA'''$: apple-green scales (Rother, *Ph.* [3] 13, 629).—$Fe(OH)Na_2A'''$: amorphous grass-green powder.—$FeNa_2H_2A'''_2$.—$FeNa_2H_2(PO_4)A'''$.—$FeA'''\,1\frac{1}{2}$aq: got by dissolving $Fe(OH)_3$ in citric acid. Light brown film.—$Fe(OH)HA'''$ 2aq (Schiff, *A.* 125, 147).—$Fe(NH_4)_3A'''_2$: greenish-yellow mass.—$Fe(NH_4)_2HA'''_2$.—$Fe(NH_4)H_2A'''_2$. $(FeO)_2(NH_4)A'''$ 4aq.—$FeA'''(NH_3)_3$ 3aq.—$Fe_2(NH_4)_2(C_6H_4O_7)_2$ 3aq (Méhu, *J.* 1873, 570).—$Fe(OH)(NH_4)_4A'''_2$ 2aq.—$Al(OH)(NH_4)_4A'''_2$.—SmA''' 6aq: amorphous pp. sol. ammonia. The ammoniacal solution does not become turbid on heating (Clève, *Bl.* [2] 43, 172).—$Y_3A'''_2$ 14aq.—$LaA'''\,3\frac{1}{2}$aq (Czudnowicz, *J.* 1860, 128; *J. pr.* 80, 31).—$CeA'''\,3\frac{1}{2}$aq.—$K_3SbA'''_2\,2\frac{1}{2}$aq: hard prisms grouped in tufts.—BiA''': granular pp. obtained by boiling bismuth nitrate with citric acid (Rother, *Ph.* [3] 6, 764; Cavazzi, *G.* 14, 289).—$(BiO)(NH_4)_2A'''$: obtained, together with the following body, by boiling the preceding with ammonia.—$(BiO)(NH_4)HA'''$.—$BiA'''4Bi(OH)_3$: gelatinous pp.—$BiA'''(NH_3)$ 3aq (Bartlett, *C. N.* 11, 28).—$FeA'''BiA'''(NH_3)_3$ 3aq.—Ag_3A''': powder; crystallises from water in needles.—Ag_2HA''' (Rönnefahrt, *J.* 1876, 562).—$Ag_3A'''(NH_3)\,1\frac{1}{2}$aq (Wöhler, *A.* 97, 18).—Ag_6A''' (?) (W.): got by heating Ag_3A''' at 100° in a current of hydrogen.—$Ag_2CaC_6H_4O_7$.—**Telluro-citrate.** $K_2A'''_2TeOH_2$ aq: leaflets, v. sol. water; formed by adding citric acid to a solution of potassium tellurite and evaporating (Klein, *C. R.* 102, 47).—**Boro-citrates.** Boro-citric acid $H_6A'''_2HBO_2$ at 80° is formed by dissolving boric acid (1 mol.) in a solution of citric acid (2 mols.). It is a deliquescent mass. The boro-citrates are formed by dissolving boric acid in solutions of the citrates. The magnesium borocitrates do not crystallise.—$Na_3A'''3HBO_2$.—$Na_2HA'''2HBO_2$.—$NaH_2A'''HBO_2$.—$K_2HA'''2HBO_2$.—$K_3A'''3HBO_2$. $KH_2A'''HBO_2$.—$KH_5A'''_22HBO_2$.—$LiH_2A'''HBO_2$.—$Li_2HA'''2HBO_2$.—$Li_3A'''3HBO_2$. $MgH_4A'''_2HBO_2$.—$Mg_2H_2A'''_24HBO_2$.—$Mg_3A'''_26HBO_2$ (Scheibe, *Ph.* [3] 11, 389).—**Aniline salt** $NPhH_2C_6H_8O_7$. Needles (Pebal, *A.* 82, 91). At 145° it changes to the phenyl-imide. **ψ-Cumidine salt** $C_6H_2Me_3NH_2H_3A'''$ [183°] (Schneider, *B.* 21, 660).

Methyl ether MeH_2A''' (Demondesir, *A.* 80, 302).

Di-methyl ether Me_2HA''' (St. Evre, *A.* 60, 325).

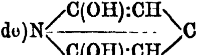
Tri-methyl ether Me_3A'''. [79°]. (c. 285°); (176° at 16 mm.). Formed, together with the two preceding bodies, by passing HCl into a solution of citric acid in MeOH (St. Evre, *C. R.* 21, 1441). Triclinic crystals. Partly split up on distillation into H_2O and tri-methyl aconitate (271°). PCl_5 gives oily $C_3H_4Cl(CO_2Me)_3$.

Acetyl-trimethyl ether $C_3H_4(OAc)(CO_2Me)_3$. (281°); (171° at 15 mm.).

Mono-ethyl ether EtH_2A'''. Formed by the action of sodium amalgam upon wet Et_3A''' (Claus a. Roennefahrt, *B.* 8, 866). Formed also by boiling citric acid with acetic ether (Kreitmair, *B.* 8, 737). Thin prisms; v. sol. water, alcohol, and ether.—Na_2EtA''' (at 100°); prisms.—Ag_2EtA'''.

Di-ethyl ether Et_2HA'''. (218°) at 60 mm. Formed, together with the preceding, by the action of sodium amalgam on wet citric ether.—$NaEt_2A'''$: deliquescent. *Formation.*—(Conen, *B.* 12, 1653; Ruhemann, *C. J.* 51, 404).

Tri-ethyl ether Et_3A'''. (218° at 60 mm.) (Ruhemann, *B.* 20, 799; *C. J.* 51, 404); (213° at 35 mm.); (263° at 300 mm.) (Conen, *B.* 12, 1653). S.G. $\frac{20}{4}$ 1·137 (C.). μ_β 1·4513. R_∞ 105·09 (Brühl). Formed by heating citric acid with alcohol and H_2SO_4, or, better, by saturating an alcoholic solution of citric acid with HCl (Thénard, *Mém. d'Arcueil*, 2, 12; Malaguti, *A. Ch.* 63, 197; Dumas, *C. R.* 8, 528; Marchand, *J. pr.* 20, 318; Heldt, *A.* 47, 157; Demondesir, *C. R.* 33, 227; Pebal, *A.* 98, 67; Claus, *B.* 8, 867). Oil; v. sol. alcohol and ether. It boils with decomposition at 280°.

Acetyl-tri-ethyl-ether $C_3H_4(OAc)(CO_2Et)_3$: (288°); (229° at 100 mm.), (214° at 40 mm.); S.G. $\frac{15}{15}$ 1·1459. By the action of strong aqueous NH_3 it is converted into the amide of di-oxy-pyridine-carboxylic acid (citrazimide)  $N\genfrac{}{}{0pt}{}{\diagup C(OH):CH \diagdown}{\diagdown C(OH):CH \diagup}C{\cdot}CONH_2$ (Ruhemann, *B.* 20, 799; *C. J.* 51, 404; *cf.* Wislicenus, *A.* 129, 175). Yields a phenyl-hydrazide [128°].

Tetra-ethyl ether $C_3H_4(OEt)(CO_2Et)_3$. S.G. $\frac{20}{4}$ 1·1022. μ_β 1·4548. R_∞ 119·97 (Brühl). Thick liquid. Bitter taste. (238° at 150 mm., and about 290° at 760 mm.). With PCl_5 it gives aconitic ether (Conen, *B.* 12, 1653).

Tri-n-propyl ether $C_3H_4(OH)(CO_2Pr)_3$. (198°) at 13 mm.

Acetyl-tri-n-propyl ether $C_3H_4(OAc)(CO_2C_3H_7)_3$. (205° at 13 mm.). When heated to 250°–280° the acetyl ethers readily split off acetic acid, yielding the corresponding ethers of aconitic acid (Anschütz a. Klingemann, *B.* 18, 1953).

Mono-isoamyl ether $C_5H_{11}H_2A'''$ (Breunlin, *A.* 91, 318). — $(NH_4)_2(C_5H_{11})A'''$. — $NaH(C_5H_{11})A'''$.—$KH(C_5H_{11})A'''$.—$Pb_3(C_{11}H_{15}O_7)_2$. $CaH_2(C_5H_{11})_2A'''_2$ *x*aq: laminæ.

Ethyl isoamyl ether $C_5H_{11}EtHA'''$. Oil.

Tri-phenyl ether $C_3H_5O(CO_2Ph)_3$. [125°]. From citric acid, phenol and $POCl_3$ (Seifert, *J. pr.* [2] 31, 470).

Mono-amide $C_3H_5O(CO_2H)_2CONH_2$. *Citromon-amic acid.* [138°]. Colourless crystals; extremely sol. water, less sol. alcohol, insol. ether and ligroin. Formed as a by-product in the preparation of the tri-amide. By boiling with HCl, or by heating with 75 p.c. H_2SO_4, it is converted into citrazinic acid $C_6H_5NO_4$.—**Salt.** $C_6H_7O_6NAg_2$: white pp.

Di-amide $C_3H_5O(CO_2H)(CONH_2)_2$: *citro-di-amic-acid*: [158°]; white plates; v. sol. water, nearly insol. alcohol and ether. Formed as a by-product in the preparation of the tri-amide. By boiling with HCl, or by heating with 75 p.c. H_2SO_4, it is converted into citrazinic acid.—$C_6H_9O_5N_2Ag$: crystalline pp.

Tri-amide $C_3H_5O(CONH_2)_3$: [210°–215°]; colourless crystals; S. (at 18°) = 2·7; (at 100°) = 33·3; insol. alcohol, ether, &c. Prepared by the action of strong aqueous NH_3 (·88) in the cold upon the tri-methyl ether of citric acid. By heating with HCl or with 75 p.c. H_2SO_4 it is converted into citrazinic acid (Behrmann a. Hofmann, *B.* 17, 2682).

Tri-methyl-amide $C_3H_4(OH)(CO.NHMe)_3$: [124°]; white prisms, v. sol. cold water.

Phenylimide $C_3H_4(OH)(CO_2H)(C_2O_2NPh)$. *Citranilic acid.* Formed by heating citric acid (1 mol.) with aniline (1 mol.) at 150° (Pebal, *A.* 82, 92). Crystalline spherules (from water).—$AgC_{12}H_{10}NO_5$.—$NPhH_2C_{12}H_{11}NO_5$.

Dianilide $C_3H_4(OH)(CO_2H)(CONPhH)_2$. [150°]. Formed by boiling the di-phenyl-amide-imide with ammonia. Concentric groups of silky needles (from alcohol).

Di-phenyl-amide-imide $C_3H_4(OH)(CONPhH)(C_2O_2NPh)$. Formed by heating the aniline salt of the phenylimide. Hexagonal plates; sol. alcohol.

Tri-anilide $C_3H_4(OH)(CONPhH)_3$. Formed by heating normal aniline citrate. Prisms (from alcohol). Insol. alkalis.

p-Tolyl-imide $C_3H_4(OH)(CO_2H)<\genfrac{}{}{0pt}{}{CO}{CO}>NC_7H_7$: [173°]; small white crystals; v. sol. alcohol, ether, and hot water, sl. sol. cold water. Formed by heating mono-*p*-toluidine citrate at 160°–170°.

Di-p-tolyl-amide-imide $C_3H_4(OH)(CO.NHC_7H_7)<\genfrac{}{}{0pt}{}{CO}{CO}>NC_7H_7$: [205°]; small granular crystals; m. sol. alcohol and ether, insol. water. Formed by heating 1 mol. of citric acid and 2 mols. of *p*-toluidine for three hours at 160°–170°.

Di-p-tolyl-di-amide $C_3H_4(OH)(CO.NHC_7H_7)_2(CO_2H)$: [161°]; small needles; sol. alcohol and ether, insol. water. Formed by heating the preceding compound with aqueous NH_3.

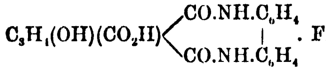
Tri-p-tolyl-tri-amide $C_3H_4(OH)(CO.NHC_7H_7)_3$: [189°]; silky white microscopic needles; sl. sol. alcohol, insol. water. Formed by heating 1 mol. of citric acid and 3 mols. of *p*-toluidine at 140°–145° (Gill, *B.* 19, 2352).

Di-ψ-cumyl-amide-imide $C_3H_4(OH)(CO.NHC_6H_2Me_3)(C_2O_2NC_6H_2Me_3)$. [173°]. The chief product of the action of ψ-cumidine (2 mols.) on citric acid (1 mol.) at 160° (Schneider, *B.* 21, 660). Prisms; v. sol. alcohol.

Di-ψ-cumidide $C_3H_4(OH)(CO_2H)(CO.NH.C_6H_2Me_3)_2$. [194°]. Formed by treating the preceding with alkalis.—NaA′. [236°].

Tri-ψ-cumidide
$C_3H_4(OH)(CO.NH.C_6H_2Me_3)_3$: [185°]; white powder, sl. sol. alcohol. Formed by heating citric acid (1 mol.) with ψ-cumidine (3 mols.).

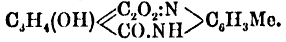
Benzidide



$$C_3H_4(OH)(CO_2H)\left\langle\begin{array}{l}CO.NH.C_6H_4\\ \qquad\quad\;|\\ CO.NH.C_6H_4\end{array}\right.$$

. From benzidine and citric acid at 150°. Carbonises above 300°. Crystalline powder.

Tolylene-diamide

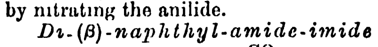


$$C_3H_4(OH)\left\langle\begin{array}{l}C_2O_2{:}N\\ CO.NH\end{array}\right\rangle C_6H_3Me.$$

[187°]. From citric acid and tolylene-diamine. [99°] at 130°. Minute crystals.

Tri-nitro-anilide
$C_3H_4(OH)(CO.NH.C_6H_4NO_2)_3$. [108°]. Formed by nitrating the anilide.

Di-(β)-naphthyl-amide-imide



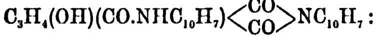
$$C_3H_4(OH)(CO.NHC_{10}H_7)\left\langle\begin{array}{l}CO\\ CO\end{array}\right\rangle NC_{10}H_7:$$

[233°]. Formed by heating 1 mol. of citric acid with 2 mols. of (β)-naphthylamine at 110°–150°. White six-sided plates. Sl. sol. alcohol, insol. water.

Di-(β)-naphthyl-di-amide
$C_3H_4(OH)(CO_2H)(CO.NHC_{10}H_7)_2$: [172°]. Formed by digesting the preceding body with conc. aqueous NH_3 at 170°. Microscopic concentric needles. Insol. water. Weak acid reaction to litmus.—A′Ag.

Tri-(β)-naphthyl-tri-amide
$C_3H_4(OH)(CO.NHC_{10}H_7)_3$: [215°]. Formed by heating the di-naphthyl-amide-imide with (β)-naphthylamine (1 mol.) at 150°–170°. Microscopic prisms. V. sol. alcohol, insol. water.

Di-(α)-naphthyl-amide-imide



$$C_3H_4(OH)(CO.NHC_{10}H_7)\left\langle\begin{array}{l}CO\\ CO\end{array}\right\rangle NC_{10}H_7:$$

[194°]. Formed by heating 1 mol. of citric acid with 2 mols. of (α)-naphthylamine at 140°–150°. Six-sided plates (from benzene). V. sol. alcohol, ether, &c., insol. HClAq.

Di-(α)-naphthyl-di-amide
$C_3H_4(OH)(CO_2H)(CO.NHC_{10}H_7)_2$: [149°]. Formed by heating the preceding body with aqueous NH_3 at 150°–160°. Small needles (from alcohol). A′Ag.

Tri-(α)-naphthyl-tri-amide
$C_3H_4(OH)(CO.NHC_{10}H_7)_3$ [129°]. Formed by heating the di-(α)-naphthyl-amide-imide with (β)-naphthylamine (1 mol.) at 150°–170°. Microscopic rhombic prisms (Hecht, *B.* 19, 2614).

ISOMERIDE OF CITRIC ACID *v.* OXY-TRI-CARBALLYLIC ACID.

CITRIDIC ACID *v.* ACONITIC ACID.

CITRONELLOL $C_{10}H_{16}O$ (Gladstone, *C. J.* 25, 47) or $C_{10}H_{18}O$ (Wright, *C. J.* 12, 318). (210°–220°). The chief constituent of the oil of citronella (*Andropogon Nardus* or *Schœnanthus*), a grass cultivated in Ceylon. P_2S_5 appears to form a mixture of terpenes and their polymerides. It combines with Br, forming a dibromide, which is split up by heat into H_2O, cymene, and HBr.

CLADONIC ACID. (β)-*Usnic acid.* [175°]. Occurs in *Cladonia rangiferina* (Stenhouse, *A.* 155, 50; Hesse, *A.* 117, 346). Yields betorcin on dry distillation. Cladonic acid is probably a mixture of usnic and barbatic acids (Paterno, *G.* 6, 113; 12, 231; Stenhouse, *A.* 203, 285).

CLASSIFICATION, CHEMICAL.—In the following article nothing more is attempted than to sketch the outlines of the methods by the employment of which a fairly satisfactory scheme of chemical classification may be attained. 'By the classification of any series of objects is meant the actual or ideal arrangement together of those which are like and the separation of those which are unlike; the purpose of this arrangement being primarily to disclose the correlations or laws of union of properties or circumstances, and secondarily to facilitate the operations of the mind in clearly conceiving and retaining in the memory the characters of the objects in question.'[1]

The importance of classification in chemistry can scarcely be too much insisted upon. The fundamental object is to arrange the various kinds of matter with which chemistry is concerned in classes, so that the connexions between the properties and the composition of these kinds of matter shall be made apparent. Inasmuch as our knowledge of the connexions between the composition and the properties of different kinds of matter is being modified from day to day, it is evident that no system of chemical classification can be regarded at present as a final system. That we may draw the outlines of a scheme of chemical classification, it is necessary first of all to inquire what the objects are which the scheme is to include.

Chemistry concerns itself with the connexions between the properties and the composition of homogeneous kinds of matter; a homogeneous kind of matter being such that all the portions, however small, into which it can be divided, are possessed of the same properties as belong to the mass. But the properties of homogeneous kinds of matter are of two kinds; on the one hand, there are those properties which belong to, or which may be acquired by, the specified kind of matter considered apart from other kinds of matter; on the other hand, there are the properties which are exhibited by the specified kind of matter when it acts on, and is acted on by, other kinds of matter. Chemistry concerns itself more especially with the latter kind of properties. Another classification of the properties of homogeneous kinds of matter may be made; we may pay regard to those properties which are the sums of the properties of the parts of the specified mass of matter; or we may look to those properties which are dependent on the configurations of these parts. Any mass of matter may be conceived to be made up of a vast but finite number of minute particles, which, for the purposes of the investigation in hand, may be regarded as indivisible. These particles may or may not be possessed of the properties which distinguish the mass of matter under consideration; the properties of the mass may be the sum of the properties of the particles, or they may differ from the sum of these properties. In the latter case we assume that the properties of the mass depend, among other conditions, on the relative arrangement of the particles. The weight of any mass of matter, *i.e.*, the force with which the matter is attracted towards the earth's centre, is absolutely independent of the arrangement of the particles, and is equal to the sum of the weights of these particles. The volumes occupied by specified masses of homogeneous gases, on the other hand, are entirely dependent on the relative arrangement of the particles, and are not the sums of the volumes occupied by these particles when separated from each other. Most of the chemical properties of any homogeneous kinds of matter are not the sums of the properties of the particles of such kinds of matter.

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[1] Stanley Jevons (in *Principles of Science*, ii. 348, 1st ed.) modifying Huxley's definition given in *Lectures on the Elements of Comparative Anatomy* (1864), p. 1.

Such then being, very broadly, the kind of properties considered in chemistry, we have next to inquire as to the meaning of the term composition. This inquiry at once carries us back to properties. Experiment shows that from certain kinds of homogeneous matter there can be obtained two or more different kinds of homogeneous matter, which new kinds of matter are wholly unlike the original in properties, and the mass of each of which is less than the mass of the original; the sum of the masses of the new kinds of matter being, however, always equal to the mass of the original matter. Experiment also shows that from certain kinds of homogeneous matter new kinds of matter can be obtained only by adding on to (or combining with) the original matter one or more different kinds of matter, and that in these cases the mass of the new kind (or kinds) of matter produced is greater than the mass of any one of the kinds of matter which have united to produce it, but is equal to the sum of the masses of all these kinds of matter. Experiment thus enables us to arrange all known kinds of homogeneous matter in two classes; those kinds belonging to the first class, *i.e.*, those from which can be obtained two or more different kinds each unlike, and weighing less than, the original, are called *compounds*; those belonging to the second class, *i.e.*, those which can be changed only by adding on to them some other kind of matter, are called *elements*. A compound may of course be changed by adding on to it a new kind of matter in the same way as an element may be changed; but an element can be changed in this way and in this way only. So far as exact knowledge goes, elements may be said to be completely homogeneous; not only are we unable to separate a specified mass of an element into particles unlike each other, by grinding, or cutting, or dividing the mass in any way, but we have every reason to suppose that the extremely minute particles of matter, by the union of which we are obliged to regard the mass as built up, are themselves completely identical in properties. Although by grinding, or cutting, or dividing by a machine, we cannot separate a specified mass of a compound into particles unlike each other, yet we are certain that the extremely minute particles of matter, by the union of which we are obliged to regard the mass as built up, are themselves built up of yet smaller particles, some of which are wholly unlike some others. But notwithstanding this distinction, which may perhaps be removed as more knowledge is gained, we are justified in applying the term homogeneous kind of matter to elements and compounds alike.

Chemistry then concerns itself with the connexions between the properties and the composition of elements and compounds. By the composition of an element is meant, at present, simply a statement of the name of the element; the element is composed of itself. By the composition of a compound is meant, at present, a statement of the elements by the union of which the compound is produced, and of the mass of each element which goes to produce a specified mass of the compound. But the word composition, as we shall see hereafter, has a fuller meaning than this.

Let us then regard the composition and properties of compounds with the view of placing together those which are like and separating those which are unlike. The moment we attempt to do this, we find that our classification of compounds must include elements also. A series of compounds may be formed by the union of one element with other elements; the properties of these compounds present some points of similarity; the presence in all of them of the specified element is accompanied by certain more or less marked similarities of properties. We wish to connect properties of compounds with composition; therefore we must learn the properties of the elements which by their union produce these compounds; but this involves the study of these elements both as they are in themselves, that is, as they are when unacted on by other elements, and also as their properties are modified when the elements combine with others. We cannot then classify compounds without studying the properties of elements, and we cannot classify elements without studying the properties of compounds.

Compounds may be classified in accordance with (1) the number of elements in each; (2) the qualitative properties of the elements in each; (3) the quantity of the elements in each; (4) the quality and quantity of the elements in each; (5) the functions performed by each; (6) the qualitative and quantitative elementary composition and at the same time the function performed by each.

Making the number of elements in each compound the class-mark, we should have a division of compounds into binary, ternary, quaternary, &c.; but this arrangement would tell very little about the compounds in each class; many compounds may be binary compounds, and yet the differences between them be very great. If the qualitative properties of the elements in a number of compounds are made the class-mark, we should have a division into compounds of oxygen, compounds of chlorine, compounds of iron, and so on; but not only would this arrangement convey little information regarding the compounds classified, but it would involve an immense number of classes, and the classes would overlap each other; *e.g.* the chlorides of iron would be placed both in the class of chlorides and also in that of compounds of iron. Nor can the quantity of the elements in compounds by itself be made the characteristic mark of a class; else we should have vast numbers of quantitative analyses as the sole basis of classification. More hopeful is it to attempt a classification of compounds based on the functions which they perform under stated conditions; this scheme leads to the placing together *e.g.* of acids, basic compounds, metallic compounds, peroxides, anhydrides, &c., &c.; but unless we connect the composition of the acids, the basic compounds, the anhydrides, &c., with the functions of each of these groups, our classification must at the best be one-sided and subject to continual modification. The characteristic mark of a class should be some property or circumstance, or a conjunction of properties or circumstances, which is easily detected, and which belongs to all the members of the class and to no others.

The property which we propose to employ as a class-mark is power of performing a stated action under stated conditions, and with this property we shall endeavour to connect a certain composition. The term composition must be interpreted as meaning not only a statement of the elements, and of the masses of these elements, which produce a specified mass of any given compound, but also a statement of the number of atoms of each element in the atomic complex or reacting chemical unit of the compound in question; or, in the case of gaseous compounds, of the number of elementary atoms in the molecule of the compound. We shall assume the molecular theory of the structure of matter, and the atomic theory of chemistry (*v.* ATOMIC AND MOLECULAR WEIGHTS, vol. i. p. 336). We shall also assume that the reader is familiar with chemical formulæ and notation.

A number of compounds exist which dissolve in water to produce more or less alkaline liquids, that is to say, liquids which exert a corroding action on organic fibres, change the tint of various vegetable colouring-matters, neutralise acids without evolution of any gas, precipitate the hydroxides of most heavy metals from solutions of salts of these metals, have a peculiar soap-like action on the skin, and saponify fats. The compounds which thus dissolve in water to produce alkaline liquids are found on analysis to be binary compounds of oxygen; the element present in combination with oxygen is in each case a metal. Other oxides exist which dissolve in water to produce more or less acidic liquids, or which can be obtained from acids, that is to say, compounds aqueous solutions of which, like alkalis, exert a corroding action on organic fibres and change the tint of various vegetable colouring-matters, which neutralise alkalis with the production of water and salts but without the evolution of any gas, neutralise carbonates of the alkali-metals with evolution of carbon dioxide, and react with many metals to produce compounds composed of the metal and a portion of the elementary constituents of the acid, this action being frequently accompanied by evolution of hydrogen. Oxides which react in this way are, generally speaking, but not always, oxides of non-metallic elements. Other oxides again exist which either do not dissolve in water, or dissolve only in relatively very large quantities of water, and which do not thus produce either alkalis or acids, but react with aqueous solutions of acids to form salts and water. Such oxides are for the most part oxides of well-marked metallic elements. Finally a few oxides exist which do not belong to any one of the three classes already considered; omitting these, the three classes of oxides may be named (1) alkali-forming or alkaline oxides; (2) acid-forming oxides or anhydrides; (3) salt-forming or basic oxides. The alkaline oxides are all oxides of metals, the acid-forming oxides are generally oxides of non-metals, and the salt-forming oxides are oxides of elements most of which are usually classed with the metals. The following list will serve as data on which a comparison of the properties with the composition of each of these classes of oxides may be based:

I. *Alkali-forming oxides.*	II. *Acid-forming oxides.*	III. *Salt-forming oxides.*
Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O; Tl_2O; MgO, CaO, SrO, BaO; (?Ag_2O?PbO)	B_2O_3; CO, CO_2; N_2O, N_2O_3, N_2O_4, N_2O_5; SiO_2; P_2O_3, P_2O_5; SO_2, SO_3; Cl_2O, Cl_2O_4; SeO_2; TeO_2, TeO_3; I_2O_5; and the following oxides of metals, viz. V_2O_4, V_2O_5; As_2O_4, As_2O_5; Sb_2O_3, Sb_2O_5; Nb_2O_5; Ta_2O_5; (?Bi_2O_5); (?Di_2O_5); CrO_3; MoO_3; WO_3; Au_2O_3; Ir_2O_3; OsO_3; PtO, PtO_2; PbO_2; MnO_2; SnO, SnO_2; TiO_2; ZrO_2.	Most of the oxides not placed in groups I. and II.; the chief exceptions being H_2O, H_2O_2, NO, and some of the oxides of Cr, Mo, W, and U. The oxides (M_2O) of Li, Na, K, Rb, Cs and Tl, and the oxides (MO) of Mg, Ca, Sr, and Ba, being already classed as alkali-forming, may be omitted from this group, although they react with acids to form salts; some metallic oxides containing relatively much oxygen, *e.g.* Na_2O_2, K_2O_4, BaO_2, Bi_2O_4, &c., form salts by the action of acids but at the same time evolve oxygen.

The alkali-forming oxides are oxides of strongly marked positive elements; if more than one oxide of such an element exists, that with the less oxygen is alkali-forming. The acid-forming oxides are either oxides of the more negative elements (non-metals), or they are the higher oxides of the less positive metals; many of the anhydrides belonging to the latter class do not form acids when acted on by water, but are obtained by removing water (usually by the action of heat) from the hydrated oxides which are themselves feebly acidic in character. By a body of a feebly acidic character is meant a compound which, as a rule, is insoluble or nearly insoluble in water, does not react with aqueous solutions of alkalis to form salts, but gives rise to the production of salts when it is fused with an alkali; the salts thus produced are unstable and are easily separated into their constituent oxides. The salt-forming oxides which are neither alkaline nor acid-forming constitute by far the greater number of the well-marked metallic oxides. The physical properties of the oxides placed in the same class are not necessarily similar; thus CO, CO_2, N_2O_4, SO_2, and some other anhydrides, are gaseous under ordinary conditions of temperature and pressure, but the metallic oxides belonging to this class are solids, many of which melt, if at all, only at high temperatures.

The division of oxides into three classes, an outline of which has now been given, is based to a great extent on the properties of compounds which are produced by the interactions of these oxides with water on the one hand, and with acids on the other hand. In order then more completely to grasp the classification of oxides it is necessary to consider the properties and the classification of alkalis, acids, and salts.

The term *alkali* was originally applied to the ashes of sea-plants; but it was soon extended to include substances which, like the ash of seaweed, easily dissolved in water to form solutions having a soap-like action on the skin, affecting the colour of many vegetable matters, and reacting with acids with effervescence and the production of new substances wherein neither the properties of the alkali nor the acid were prominent. About the middle of the eighteenth century Black proved by quantitative experiments that the effervescence which occurs during the interaction of an acid and an alkali is caused by the outrush of a gas which existed in the alkali in combination with the other constituents of that body. That the same gas may also be obtained from the alkali by the action of heat was also proved by Black. From this time it became customary to distinguish mild or carbonated alkali from burnt or caustic alkali, the former being regarded as a combination of the caustic alkali with carbonic acid gas. Both carbonated and caustic alkali reacted with acids to produce the same substance, in which the properties of alkali and acid were lost, or rather merged into a new set of properties; the action was attended in the case of carbonated alkali with evolution of carbonic acid gas, but in the case of caustic alkali no gas was produced. Continued examination of alkali showed that the composition of the substance thus named was not always the same; this led to the recognition of more than one kind of matter exhibiting the characteristic properties of alkalis. Lavoisier adduced reasons for regarding the various alkalis as compounds of unknown metals with oxygen, but he did not succeed in actually demonstrating their composition. In 1807 Davy decomposed two alkalis, potash and soda, each into oxygen and a metal, by passing an electric current through them when molten, and a year later by the same agency he separated the three earthy bodies, lime, strontia, and baryta —bodies which to a great extent resemble alkalis in their properties—into oxygen, and in each case a metal. The composition of the various bodies having the properties already summarised as characteristic of alkali was now settled; these bodies were oxides of metals. But further investigation showed that aqueous solutions of these metallic oxides did not contain the oxides, but rather compounds of metal, oxygen, and hydrogen, and that these compounds, these hydroxides, were obtained as definite well-marked solid bodies by boiling off the water from the solutions in question. Now as the characteristic properties of alkali belonged to aqueous solutions of the metallic oxides under consideration it was better to apply the name alkali to the hydroxides rather than to the oxides of certain metals. The composition of alkalis is represented by the formula MOH, where M = Li, Na, K, Rb, Cs, or the compound radicle NH_4; each of these compounds, except NH_4OH, is known as a definite solid body. An aqueous solution of ammonia, NH_3, reacts towards vegetable colouring-matters, towards acids, towards solutions of the salts of iron, copper, bismuth, tin, and many other heavy metals, in a manner very similar to that in which aqueous solutions of the five alkaline hydroxides, MOH, react towards these classes of substances. The salts formed by the action of acids on the hydroxides in question are generally isomorphous with, and in other properties similar to, the salts formed by the action of the same acids on an aqueous solution of ammonia. For these and a few other reasons the composition of an aqueous solution of ammonia, NH_3, is supposed to be similar to that of aqueous solutions of the solid alkalis; but the compositions of the latter solutions are represented by the symbols LiOHAq, NaOHAq, &c., therefore the composition of the former solution is represented by the symbol NH_4OHAq. As we have hydroxides of the metals lithium, sodium, potassium, &c., so we have a hydroxide of the compound radicle ammonium (NH_4); the former hydroxides are stable solid bodies, the latter exists only in aqueous solution (*v.* AMMONIUM COMPOUNDS, vol. i. p. 200). The hydroxides MO_2H_2 where M is Mg, Ca, Sr, or Ba, all more or less resemble the alkalis; these hydroxides are white solids, which require for solution much larger relative quantities of water than are needed to dissolve equal masses of the alkalis, but which thus produce solutions capable of neutralising acids without effervescence, of changing vegetable colouring-matter in the same way as solutions of the alkalis, of precipitating oxides or hydrated oxides of many heavy metals from solutions of the salts of these metals, of corroding organic fibres to some extent, of saponifying fats, and of quickly combining with carbonic acid to produce carbonates. As all the alkalis and the four compounds of Mg, Ca, Sr, and Ba, just mentioned are compounds each of oxygen, hydrogen, and a metal, and as many other metallic hydroxides, *e.g.* CuO_2H_2, $Fe_2O_6H_6$, &c. &c., do not exhibit alkaline properties, it seems probable that the alkaline qualities of the hydroxides of Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba, are to be associated with the properties of the metals, Li, Na, K, . . . Ba.

Thus in our attempts to classify oxides we are obliged to have regard, first, to the properties of alkalis, and then to the properties of the elements of which these alkalis are composed. What, then, are the properties of the metals Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba?

The metals Li, Na, K, Rb, and Cs, are silver-white solids, with low melting-points, and very small specific gravities (Li, Na, and K, being lighter than water); the metals are extremely easily oxidised, the process of oxidation being attended with production of much heat; they rapidly decompose cold water with evolution of half the hydrogen of the water decomposed and production of hydroxides MOH which remain in solution; during this process much heat is produced. The metals easily and rapidly combine with the halogens and with sulphur; they are electro-positive to all other metals, and the most electro-positive metal of the group is that with the largest atomic weight (Cs). The compositions of the chief compounds of these metals are represented by the symbols M_2O, MOH, M_2S, MSH, MX ($X = Cl, Br, I, F, CN$), M_2SO_4, $MHSO_4$, MNO_3, M_2CO_3, $MHCO_3$, &c., where $M = Li, Na, K, Rb$, or Cs. These compounds are for the most part white and easily soluble in water; many of them are not chemically changed by the action of heat alone; all compounds of similar composition, *e.g.* all M_2SO_4 or all MCl, are as a rule isomorphous; the sulphates M_2SO_4 form alums by combination with sulphates of the composition M_23SO_4 where $M = Fe, Al, Cr, In$, or Ga. The properties of the hydroxides MOH have already been detailed.

The metals Ca, Sr, and Ba are whitish-yellow solids, the melting-points of which have not been accurately determined, but are somewhere about a red heat; the specific gravities of these metals are represented by small values, which are, however, decidedly greater than those that represent the specific gravities of the metals Li . . . to Cs; these metals are harder than the alkali metals, but, compared with the group of metals as a whole, they are soft; they quickly oxidise in air or oxygen, and decompose cold water with production of much heat, evolution of half the hydrogen of the water decomposed, and formation of solutions of the hydroxides MO_2H_2. In the cases of Li . . . Cs one atom of metal reacts with one molecule of water evolving one atom of hydrogen, in the cases of Ca . . . Ba one atom of metal reacts with two molecules of water evolving two atoms of hydrogen; the metals, so far as exact experiment goes, seem to combine easily and rapidly with the halogens and with sulphur; they are electro-negative to the metals Li . . . Cs, but positive to all other metals. The compositions of the chief compounds of these metals are represented by the symbols MO, MO_2H_2, MS, MS_2H_2, MX_2 ($X = Cl, Br, I, F, CN$), MSO_4, $M2NO_3$, MCO_3, &c., where $M = Ca, Sr$, or Ba. Most of these compounds are white; the oxides and hydroxides are not very soluble, the sulphates and carbonates are nearly insoluble, the chlorides and nitrates are easily soluble, in water; the hydroxides, nitrates, and carbonates are decomposed by the action of heat alone; almost all similar compounds are isomorphous; the sulphates do not form alums, nor do the compounds generally exhibit any marked tendency to form double or basic salts. The properties of the hydroxides have already been detailed.

The metal magnesium is a silver-white solid, the melting-point of which is about 500°–700° (not accurately determined), and the specific gravity is a little greater than that of calcium; the metal is much more malleable and ductile than Li . . . Cs or Ca . . . Ba; it is scarcely oxidised by exposure to air or oxygen at ordinary temperatures, but when rapid oxidation is begun by heating the metal in air or oxygen it proceeds with production of much heat and light. Magnesium decomposes water at 100° very slowly with formation of MgO_2H_2; it does not act chemically on cold water; it does not combine with the halogens or with sulphur at ordinary temperatures. The compositions of the chief compounds of this metal are represented by the symbols MgO, MgO_2H_2, MgS, MgX_2 ($X = Cl, Br, I, F, CN$), $MgSO_4$, $Mg2NO_3$, $MgCO_3$, &c. Most of the compounds are white; the oxide and hydroxide are only very slightly soluble in water; the oxide combines with water to form MgO_2H_2, but much less heat is produced during this process than when CaO, SrO, or BaO, combines with water to form the hydroxide. The hydroxide is easily decomposed by heat alone into oxide and water; the sulphate, nitrate, and haloid salts are easily soluble in water, the carbonate is nearly insoluble in water; many compounds of magnesium salts with those of the alkali metals, &c., are known; some of the magnesium compounds are isomorphous with the similar compounds of Ca, Sr, and Ba, but the isomorphism of the two series of salts is very far from being complete. (For more details of the properties of the three classes of metals *v.* Alkalis, metals of the, vol. i. p. 114; Alkaline earths, metals of the, vol. i. p. 112; and Magnesium metals.)

These facts concerning the metals whose hydroxides are the alkalis, and concerning those whose hydroxides more nearly approach the alkalis than do the hydroxides of any other elements, show that the property of forming an alkaline hydroxide is accompanied by the following properties on the part of an element: low specific gravity, not very high melting-point, small malleability and ductility, softness, occupation of a very positive position in the electrical series of elements, power of rapidly decomposing water with evolution of part of the hydrogen thereof, power of forming salts which are not easily decomposed by heat alone, and many of which are easily soluble in water, great readiness to combine with oxygen and with the halogens. Of all the metals whose properties we have considered in detail, magnesium differs most from the ideal alkali-forming metal; but the hydroxide of magnesium is decidedly less markedly alkaline than the hydroxide of any other metal in the two groups from Li to Sr.

When a given element exhibits a fair number of the properties given above as characteristic of the alkali forming elements we may conclude that the hydroxide of that element will be more or less alkaline in its properties. There is a certain element characterised by the following properties: specific gravity large (11·9), melting-point moderately low (290°), very soft, malleability and ductility moderate, oxidises rather rapidly in air but action soon stops because of formation of film of oxide, burns rapidly in oxygen at about 300°, does not decompose water until a red-heat is reached; less positive than zinc, which is again less positive than Ca, Sr, or Ba; combines readily with the halogens and with sulphur; most of the salts of this metal are white and easily soluble in water, some of them are isomorphous with, and of similar composition to, salts of potassium. In many respects then this metal approaches the ideal alkali-forming element; but in others, notably its high specific gravity and comparatively negative position in the electrical series, it departs from the alkali-forming type. We should expect the oxide and hydroxide of this metal to present fairly close resemblances to the corresponding compounds of the lithium group of metals, but at the same time to show considerable differences from these compounds. As a matter of fact, the metal forms two oxides and two hydroxides; one pair of these compounds shows close analogies with the corresponding compounds of the alkali metals; the other pair shows fairly marked analogies with the corresponding compounds of aluminium. The metal in question, which is thallium, belongs to two groups of elements; it forms an alkaline oxide and hydroxide Tl_2O and $TlOH$, and another oxide and hydroxide Tl_2O_3 and $TlO.OH$.

Having thus learnt something regarding the properties and compositions of alkalis, let us turn to the second group of compounds which it is necessary to consider before we can complete the classification of oxides; let us briefly consider the group of *acids*. The name *oxygen* perpetuates the Lavoisierian conception of the composition of acids: this element was for Lavoisier emphatically *the* acid-producer. The products of the combustion in oxygen of sulphur, phosphorus, carbon, boron, nitrogen, selenion, and a few other elements, dissolve in water to form solutions which have 'acid reactions,' that is to say, have a sour taste, corrode organic fibres, change the tint of many vegetable colouring-matters, neutralise alkalis with production of salts and water, and dissolve many metals with evolution of gas (generally hydrogen). By removing water from these solutions, at least one definite compound can in most cases be obtained, composed of the element which had been burnt in oxygen, combined with oxygen and hydrogen; when this compound is again dissolved in water the original acid liquid is reproduced. Very many other compounds are known which form aqueous solutions characterised by acidic reactions as above enumerated; most of these compounds are composed of oxygen, hydrogen, and a third element. On the other hand, very many compounds formed by the union of oxygen, hydrogen, and a third element do not form acidic solutions when dissolved in water; and, finally, a few compounds are known, aqueous solutions of which are most definitely acidic, but which do not themselves contain oxygen. Oxygen is therefore not the sole acid-producing element; but the fact remains that by far the greater number of acids are composed of oxygen united with other elements.

Putting into one class all those compounds which dissolve in water with formation of solutions having acidic properties, as these have been already enumerated, and then tabulating the composition of these compounds, it becomes evident that they are all compounds of hydrogen with one or more other elements. Hydrogen then, rather than oxygen, would seem to be the acid-producing element. But further examination of the compounds of hydrogen shows that very many of these are not possessed of any of the characteristics of acids.

Is it possible then to trace any definite connexion between the composition of compounds and the possession or non-possession by them of acidic properties? In attempting to answer this question we are confronted with the great difficulty of chemical classification. We cannot define the class acids, just as we could not define the class alkalis: an ideal acid or alkali may be defined, but it is necessary to place in one or other of these classes many bodies which possess some of the properties of the ideal type, but in other properties diverge more or less widely from that type. Chemical classification based on the notion of connecting properties with composition, is at best a typical classification, and such a system cannot be regarded as final in an exact science. The mark of a class should be some property or circumstance, or conjunction of these, which is clear and definite, and which belongs to all the members of the class and to no other bodies. But we cannot predicate any one property of acids which is perfectly clear and definite, and the possession or non-possession of which shall determine whether a specified compound is or is not to be admitted to this class. The reaction which occurs between an acid and a metallic hydroxide, or hydrated oxide, more nearly approaches to a good class characteristic than any other single property of acids. The products of the action in question are water and a compound formed of the metal of the hydroxide employed, and the elements of the acid excepting the whole or a part of the hydrogen; such a compound is called a *salt*. The following equations, representing the distribution of the elements of the reacting compounds before and after the mutual actions of various acids and metallic hydroxides, will illustrate, more clearly than can be done in words, the characteristic reaction of an acid:—(the symbol Aq is used to denote that the compound which it follows is dissolved in water)

1. $HClAq + NaOHAq = NaClAq + H_2OAq.$
2. $HNO_3Aq + TlOHAq = TlNO_3Aq + H_2OAq.$
3. $H_2SO_4Aq + KOHAq = KHSO_4Aq + H_2OAq.$
4. $H_2SO_4Aq + 2KOHAq = K_2SO_4Aq + 2H_2OAq.$
5. $H_2SO_4Aq + CuO_2H_2 = CuSO_4Aq + 2H_2OAq.$
6. $2H_4C_2O_2Aq + PbO_2H_2 = Pb(H_3C_2O_2)_2 + 2H_2OAq.$
7. $H_4C_2O_2Aq + NaOHAq = NaH_3C_2O_2Aq + H_2OAq.$
8. $H_3PO_4Aq + TlOHAq = TlH_2PO_4Aq + H_2OAq.$
9. $2H_3PO_4Aq + Fe_2O_6H_6 = 2FePO_4 + 6H_2OAq.$
10. $H_2C_2O_4Aq + CaO_2H_2Aq = CaC_2O_4 + 2H_2OAq.$

An acid, then, may be provisionally defined as a compound of hydrogen with another element, or other elements, which, when dissolved in water, reacts with metallic hydroxides to produce water and a salt; a salt being a compound formed by the union of the elements of the acid, excepting the whole or a part of the hydrogen, with the metal of the metallic hydroxide. This definition is more commonly put into the shorter form, an acid is a compound containing *replaceable* hydrogen; but unless a definite meaning is given to the expression replaceable hydrogen, the definition of acid means nothing: the meaning of the words *replaceable hydrogen* is given in the longer definition of acid stated above. It is found that most compounds which are acids, in accordance with the provisional definition we have adopted, when dissolved in water form more or less corrosive liquids, which affect vegetable colouring matters, have a sour taste, and dissolve many metals with formation of salts and evolution of gas, which is usually hydrogen. But, on the other hand, some compounds which are possessed of many of the properties just detailed do not react with metallic hydroxides to form salts; and, further, some compounds which are not possessed of any of the properties detailed do react with metallic hydroxides to form salts (*v.* ACIDS, vol. i. p. 47).

Looking at the composition of compounds which undoubtedly come under the definition of acid, and which at the same time are characterised by the other four properties enumerated, we find that the elements, or some of the elements, which by their union with hydrogen form the acid, are strongly negative in character; in other words, the element or elements other than hydrogen more or less resemble oxygen in their general chemical characteristics. As a whole, the elements which are classed as non-metallic are those which by union with hydrogen, and generally with hydrogen and oxygen, produce acids. When an acid is a compound of a metal united with hydrogen and another element or elements, for no binary metallic compound is acidic, that other element is always very negative. The following list exhibits most of the well-marked metallic acids which have been obtained in approximate purity:—

Acids containing metals.

H_3AsO_4	H_2SnO_3	H_2SnS_3
$HAsO_3$	—	—
$H_4As_2O_7$	(?H_2PbO_3)	(?H_3AsS_4)
—		—
H_3SbO_3	H_2CrO_4	$H_4Fe(CN)_6$
H_3SbO_4	...	$H_3Fe(CN)_6$
$HSbO_3$	(?$H_2Mn_2O_8$)	&c.
	—	(?H_2PtCl_6)
$H_4Sb_2O_7$	H_2MoO_4	(?$HAuBr_4$)
—	—	(?$HAuCl_4$)
HVO_3	H_2WO_4	
	—	
$H_4V_2O_7$	H_2UO_4	
—	-	
$H_4Ta_2O_7$	(?$H_2M_2O_7$?$H_2M_3O_{10}$	where M = Mo, W, or U.)
—		
(?H_2TiO_2 ?H_4TiO_4)	—	
	H_2PtO_2	
—	—	

The element which is generally combined with hydrogen and a metal in these acids is oxygen: in a few acids sulphur, in (?) three acids chlorine or bromine, and in a few acids the negative group CN is combined with hydrogen and a metal. It is also to be remarked that the metals which form well-marked acids by union with oxygen and hydrogen are those which, compared with the majority of the metals, are negative.

The general conclusion to be drawn from the facts now reviewed concerning the connexions between the properties and the composition of acids is, that those compounds which are decidedly acidic in properties, as the term acidic properties has been defined, are formed by the union of hydrogen with one or more decidedly negative elements. Acids are seen to be strongly contrasted with alkalis, both in properties and composition.

Oxides were divided (*v.* p. 198) into three groups: alkali-forming, acid-forming, and salt-forming, oxides. We can now understand in a general way what is meant by an alkali-forming oxide, or by an acid-forming oxide; it remains to consider the meaning of the term salt-forming as applied to oxides. At the outset, let us remark that a salt-forming oxide may also be acid-forming, and that an alkali-forming oxide also is salt-forming. In considering the meaning of the term salt-forming oxide, it will therefore be necessary to study those typical compounds which possess the property in question to a marked extent. A salt has been already stated to be one of the products of the mutual action of an acid and a metallic hydroxide or hydrated oxide, and to be composed of the elements of the acid, excepting the whole or part of the hydrogen, united with the metal of the metallic hydroxide. It is impossible to generalise the properties of salts; many of them are soluble in water, some are insoluble; aqueous solutions of many exhibit acidic reactions, aqueous solutions of others exhibit alkaline reactions, and aqueous solutions of very many are neutral, *i.e.* exert no corroding action on organic fibres, have no sour or soap-like taste, do not affect vegetable colouring-matter, do not saponify fats, do not dissolve metals, or react with metallic hydroxides, &c. We must be content to look at the composition and the conditions of formation of salts. The composition of salts, regarding them as derivatives of acids, has already been stated. But salts are formed in other ways; they are sometimes produced by the mutual action of an acid-forming oxide and an oxide containing much oxygen, called a peroxide – *e.g.* $BaO_2 + SO_2 = BaSO_4$; sometimes by the action of a salt-forming oxide on an aqueous solution of another oxide from which an acid has not actually been obtained, thus $K_2O + CO_2Aq = K_2CO_3Aq$; sometimes by fusing together a metallic and a non-metallic oxide, *e.g.* $CaO + SiO_2 = CaSiO_3$; sometimes by dissolving the sulphide of a less positive metal in a solution of the sulphide of a very positive metal, thus $As_2S_3 + K_2SAq = 2KAsS_2Aq$, or $WS_3 + K_2SAq = K_2WS_4Aq$; and sometimes in other ways. The products of such actions as these are called salts, either because they can also be directly obtained by the mutual actions of acids and metallic hydroxides, or because they are composed of positive elements (metals) combined with negative elements, of which oxygen is usually one, and which negative elements are known to form acids by union with hydrogen, although the special acid of which any one of these specified salts is theoretically a metallic derivative may not have been prepared. All oxides are in a sense salt-forming; an alkaline oxide reacts with water to form an alkali, and the alkali reacts with an acid to form a salt; an anhydride reacts with water to form an acid, and by the mutual action of this acid and an alkali a salt is produced. But placing on either side those oxides which have been already classed as alkali-forming, and those which have been classed as acid-forming, there remain a great many oxides which are emphatically salt-forming oxides. As a class, these oxides form salts by reacting either with acids or with solution of oxides which act as if they contained acids, although no acid may actually be obtained when the dissolving water is removed, or, lastly, by reacting in the liquid state (not in solution) with the oxides of non-metals or of the more negative metals; examples of these three types of action are exhibited by the following processes:—

(1) $CuO + H_2SO_4Aq = CuSO_4Aq + H_2OAq$,
(2) $BaO + CO_2Aq = BaCO_3 + Aq$,
(3) $K_2O + Ta_2O_5(\text{fused}) = 2KTaO_3$.

Some salt-forming oxides also produce salts, either by dissolving in concentrated solutions of alkalis, or by combining with alkalis when melted in contact with them; thus freshly ppd. aluminium oxide dissolves in solution of acids to form salts, and also in a concentrated aqueous solution of potash to form a salt; the two actions may be represented thus:

(1) $Al_2O_3 + 6HClAq = Al_2Cl_6Aq + 3H_2OAq$,
(2) $Al_2O_3 + 2KOHAq = Al_2O_4K_2Aq + H_2O$.

Again, moist SnO_2 dissolves in concentrated aqueous potash to form a solution of potassium stannate K_2SnO_3, but the same oxide dissolves in hydrochloric acid to form stannic chloride, $SnCl_4$; inasmuch as the acid H_2SnO_3, of which SnO_2 is the anhydride, is known, we have in stannic oxide, SnO_2, an example of a compound which is at once an acid-forming and a salt-forming oxide. The oxide MnO_2 dissolves in molten KOH to form the salt potassium manganate, K_2MnO_4; the same oxide, when produced in a concentrated solution of lime, combines with the lime to form a series of salts, of which $CaMnO_3$ may be taken as a representative; and, lastly, the same oxide, when hydrated, dissolves in strong sulphuric acid to form a sulphate of manganese $MnO_2.2SO_3$. This oxide, MnO_2, thus exhibits some of the properties of two of the three classes into which we have divided oxides.

We began by proposing to arrange oxides in three classes in accordance with certain prominent reactions of these oxides; that we might attach to the reactions in question such definite meanings as should suffice for classificatory purposes, we were obliged to consider the meaning of the terms which summarise the reactions and composition of three other groups of compounds - acids, alkalis, and salts; that we might grasp the significance of these terms, we had to turn from compounds to elements, and roughly to classify these in accordance with their acid-forming or alkali-forming functions; but we found all this scheme of classification to be based at once on the composition and the functions of the bodies classified, and the word function we were obliged to interpret as implying the notion of mutual action and reaction between at least two kinds of matter. We arrived at no perfectly clear definition of any one of the classes of compounds under examination; we did succeed in conceiving the properties and the composition of a typical acid-forming, alkali-forming, and salt-forming, oxide; but when we applied this conception, gained, it is to be remarked, from the study of actual acid-, alkali-, and salt-forming oxides, to individual compounds, we found that very few of these exhibited all the characteristics which we had laid down as marking off the typical acid-forming from the typical alkali-forming, or both from the typical salt-forming, oxide.

Looking back for a moment at the classification of oxides, and considering what it implies, one thing stands clearly out, namely, that this classification of oxides carries in itself a classification of elements. Those elements which form markedly alkaline oxides fall into one class, those which form oxides which are distinctly anhydrides fall into a second class, and a third class includes those elements the best-marked oxides of which are neither alkali-forming nor acid-forming, but salt-forming. Or, putting the matter in even more general terms, the classification of oxides suggests a means of classifying the elements. Let us put into one class all the elements which, under similar conditions, form compounds similar in composition and function. Let us then examine the elements in a class with the view of finding whether they do or do not exhibit similarities in physical properties. If the result is fairly successful, let us examine more closely into the composition of the compounds belonging to specified classes, and endeavour to learn something of the structure of these compounds in the light which is thrown on structure by the molecular and atomic theory. Finally, let the knowledge which may thus be gained of structure react on that previously amassed concerning function, that by the help of both some advance may be made in finding a solution for the fundamental problem of chemistry, which is, to trace the connexions between changes of composition and changes of properties in homogeneous kinds of matter.

Instead of following the course of this investigation step by step, it will be more advantageous to begin with the leading principle, which has been gained after much laborious inquiry. In the article ATOMIC AND MOLECULAR WEIGHTS a sketch was given of the *periodic law*. The substance of that sketch it would be needless to repeat here; let us rather apply it to the point in hand, namely, the classification of the elements, remembering always that a good classification of elements implies and carries with it a good classification of compounds also.

The classification founded on the periodic law arranges the elements in *groups* and *series* (*v.* vol. i. p. 351); the members of the same group more or less closely resemble each other; the properties of the members of a series vary from member to member so that the last, that is the element with the largest atomic weight, is more unlike the first than any other member of the series. Each series to some extent repeats the characteristics of that which precedes it. The properties of an individual element are chiefly conditioned by (1) the group, (2) the series, to which it belongs, (3) its position in the group and in the series, (4) its relations to elements situated similarly to itself in other groups and series, and (5) the relations of the group and of the series to other groups and series. As regards the characteristics of individual groups and series, and the relations between various groups and series, it should be remarked, (1) that each group is made up of elements belonging to even series and elements belonging to odd series; (2) that an odd and an even series together comprise 14 elements, and that in the cases of series 4 and 5, 6 and 7, and 10 and 11, there is a group of three elements (Group VIII.) forming what is called by Mendelejeff a 'transition-period' from the even to the odd series; (3) that there is certainly no such 'transition-period' connecting series 2 and 3, but that very probably such a period of three elements will be discovered between series 8 and 9; (4) that the elements in the even series, or in the odd series, of any group are more like one another than elements in the even are like those in the odd series; (5) that, omitting series 2 and 3, the passage from an even to an odd series is accomplished by a gradual change of properties, but the passage from an odd to an even series by a more sudden change of properties; (6) that the distinctly non-metallic elements occur in odd series, except in the case of series 2; (7) that, omitting series 2, easily gasified organo-metallic compounds, so far as data go at present, are formed only by elements which occur in odd series; (8) that the properties of hydrogen are so marked, and are typical of such diverse elements, that it is placed in a series [series 1] by itself; (9) that all the members of series 2 [Li to F], and at least the first member of series 3 [Na], are to a great extent marked by peculiar properties, and that the relations of these elements to those in series 4, and in the case of sodium to series 5, are rather markedly different from the normal relations of an odd series to the next odd series, or of an even series to the next even series. The elements Li to Na have been called by Mendelejeff 'typical elements.' The following table (copied with a few changes from one given by Mendelejeff) exhibits the arrangement of the elements in groups and in odd and even series (at. wts. in round numbers):—

The even series elements in this group are beryllium, calcium, strontium, and barium. The three metals, Ca, Sr, and Ba, are yellowish-white, rather soft, solids, with comparatively small specific gravities; their characteristic properties have already been detailed in the present article (*v.* p. 200). The metal beryllium differs considerably from the other even series members of the group; unlike these metals, it cannot be obtained by electrolysing the chloride; the method by which beryllium is obtained is very similar to that whereby magnesium is prepared, viz. by heating the chloride with metallic sodium. Beryllium appears to be a silver-white, hard, solid; its specific gravity is small (approximately 1·7), melting-point high, not accurately determined, but certainly above 600°; the specific heat of this metal increases rapidly as temperature rises, and approaches a constant value between 400° and 500°. The spectrum of beryllium more nearly resembles that of lithium than of any other element, in the number, relative position, and intensity, of the lines; but the character of the lines of greatest intensity in the beryllium spectrum closely resembles that of two pairs of lines in the spectrum of calcium. This metal does not oxidise in air at ordinary temperatures, and even when heated in oxygen it is only superficially oxidised; it combines with chlorine and iodine only at high temperatures; when heated with sulphur, no sulphide of beryllium is formed; it very readily combines with silicon. Beryllium does not decompose water even at a red heat; it dissolves in an aqueous solution of potash with formation of beryllium oxide and evolution of hydrogen; it is easily soluble in dilute hydrochloric or sulphuric acid, but has little or no action on nitric acid. The compositions of the salts of beryllium are represented by the same formulæ as express those of the salts of Ca, Sr, and Ba; the oxide BeO does not combine with water, but the hydroxide, BeO_2H_2, can be prepared indirectly; this hydroxide is easily decomposed by heat alone, it resembles the hydroxides of zinc and of aluminium in being soluble both in acids and in aqueous potash, it combines with carbon dioxide to produce $BeCO_3$; the oxide crystallises in the same (hexagonal) form as aluminium oxide; under certain conditions zinc oxide can also be obtained in this form; beryllium oxide usually occurs in combination with

	Series							
Groups	1		2	4	6	8	10	12
I.		Typical Elements	Li = 7	K = 39	Rb = 85	Cs = 133	—	—
II.			Be = 9	Ca = 40	Sr = 87	Ba = 137	—	—
III.			B = 11	Sc = 44	Yt = 89	La = 139	Yb = 173	—
IV.			C = 12	Ti = 48	Zr = 90	Ce = 140	—	Th = 232
V.			N = 14	V = 51	Nb = 94	Di = 144	Ta = 182	—
VI.			O = 16	Cr = 52	Mo = 96	–	W = 184	U = 240
VII.			F = 19	Mn = 55	–		—	—
VIII.				Fe = 56 Ni = 58·6	Rh = 104 Ru = 104·5	– —	Os = 191 Ir = 192·5	— —
				Co = 59 Cu = 63	Pd = 106 Ag = 108		Pt = 194·5 Au = 197	—
I.	H = 1		Na = 23	Cu = 63	Ag = 108	–	Au = 197	—
II.			Mg = 24	Zn = 65	Cd = 112	—	Hg = 200	—
III.			Al = 27	Ga = 69	In = 114	—	Tl = 204	—
IV.			Si = 28	Ge = 72	Sn = 118	—	Pb = 207	—
V.			P = 31	As = 75	Sb = 120	Er = 166	Bi = 208	—
VI.			S = 32	Se = 79	Te = 125	—	—	—
VII.			Cl = 35·5	Br = 80	I = 127	—	—	—
	1		3	5	7	9	11	13
	Series							

As regards the mutual relations of groups and series, it should be further remarked that, calling the even series members of a group a family, and the odd series members a family, in groups 1 and 7 the family-character is more marked than the group-character, in groups 3, 4, and 5 the group-character preponderates over the family-character, and in groups 2 and 6 the two characters are about balanced, so that these two groups present, perhaps, the best examples for the detailed study of the application of the periodic law to the classification of elements. Group II. contains the following elements:—

Group II.

Even series:

2	4	6	8	
Be = 9	Ca = 40	Sr = 87	Ba = 137	

Odd series:

3	5	7	9	11
Mg = 24	Zn = 65	Cd = 112	—	Hg = 200

alumina and silica, as beryl. Most of the salts of beryllium are white; the nitrate, sulphate, and chloride are soluble, the carbonate and phosphate are insoluble, in water. Beryllium sulphate does not form an alum, but does combine with potassium sulphate to form a double salt having the composition $BeSO_4.K_2SO_4.2H_2O$: the chloride does not form double salts with the alkali chlorides; the carbonate is fairly stable towards heat, but easily forms basic, and also double, salts; the sulphate, which also readily produces basic salts, is completely decomposed into oxide and oxide of sulphur by the action of heat alone. The chloride and bromide of beryllium have been gasified; an ethide, $Be(C_2H_5)_2$, is known; it is a fuming liquid which takes fire when gently warmed in air.

The odd series members of the group we are considering are magnesium, zinc, cadmium, and mercury. The properties of the metal magnesium have already been stated in this article (*v.* p. 200); of the remaining metals, zinc and cadmium are very similar, while mercury differs in many respects from any other member of the group. Zinc and cadmium occur together in minerals, chiefly as sulphides; both are obtained by deoxidising the oxides by hot carbon; both are heavy, moderately hard, tin-white solids (S.G. Zn = 7·2, S.G. Cd = 8·6); both melt at fairly high temperatures (M.P. Zn = 420°, M.P. Cd = 320°), and both can be volatilised at temperatures somewhat under 1000°. Cadmium is ductile and malleable, the ductility and malleability of zinc vary considerably with variations of temperature; both are easily soluble in the ordinary mineral acids, zinc dissolves in concentrated warm aqueous solutions of potash or soda, with evolution of hydrogen and production of an unstable zincate of the alkali metal (xZnO.yM$_2$O); both are nearly unacted on by air or oxygen at ordinary temperatures, but are rapidly burnt to oxides when heated in oxygen; both readily combine with the halogens and with sulphur. The formulæ which represent the compositions of the chief compounds of Be, Ca, Sr, Ba, and Mg, also represent those of the chief compounds of Zn and Cd; almost all similar salts of Zn and Cd are isomorphous. The oxides, MO, do not combine with water to form hydroxides; the hydroxides, MO_2H_2, are quite insoluble in water, and are readily decomposed by heat alone into oxides and water; ZnO_2H_2 is soluble, CdO_2H_2 is insoluble, in aqueous potash. The chloride, sulphate, and nitrate of either metal is soluble, the phosphate and carbonate are nearly, if not altogether, insoluble, in water; these salts show great readiness to form double salts, especially with the alkali metals and with ammonia, and also to form basic salts, but the zinc salts are more ready to undergo the latter changes than the salts of cadmium. Mercury differs from all other metals in being liquid at temperatures above −39°. This metal occurs chiefly as sulphide, from which it may be obtained by heating with iron, and in other ways; it is a silver-white, heavy liquid (S.G. about 13·5); it boils at 350°, and is very easily volatilised; it is unacted on by oxygen until a temperature near 350° is reached, when it slowly combines with oxygen to form HgO. Mercury readily combines with the halogens and with sulphur; it is without action on water; dilute nitric acid quickly dissolves mercury, and it is also soluble in hot concentrated sulphuric acid, but neither boiling hydrochloric, nor boiling dilute sulphuric, acid acts upon it. Mercury forms two series of salts, mercurous salts represented by Hg_2O, Hg_2Cl_2, Hg_2SO_4, $HgNO_3$, &c., and mercuric salts represented by HgO, $HgCl_2$, $HgSO_4$, $Hg2NO_3$, &c.; the latter, as a class, are more soluble in water, and are much more stable, than the former. No hydroxides of mercury are known; HgO is said to be very slightly soluble in water, and also in molten potash. The salts of mercury, especially the mercuric salts, form a great many double compounds, chiefly with the salts of the alkali metals; they also readily form many basic salts; a very large number of compounds of mercury salts with ammonia, and derivatives of ammonia, is known.

The following data present some of the measurements which have been made (chiefly by Thomsen) of the quantities of heat produced during similar changes undergone by the elements, or by compounds of the elements, in the group we are now considering:—[1]

M	$[M,Cl^2,Aq]$	$[M,Br^2,Aq]$	$[M,I^2,Aq]$	$[M,O,N^2O^5Aq]$	$[M,O]$
Ca	187,600	165,800	135,300	177,160	130,930
Sr	195,700	173,800	143,400	185,410	128,440
Ba	196,300	174,400	144,000	187,000	124,240
Mg	186,900	165,000	134,600	176,480	146,000
Zn	112,800	90,900	60,500	102,510	85,400
Cd	96,300	74,400	44,000	86,000	65,600
Hg	53,200[2]	41,180[2]	21,300[2]	37,070	30,670
Hg_2	62,600[2]	50,950[2]	28,400[2]	47,990	42,200

M	$[M,Cy^2,2KCyAq]$
Zn	62,230
Cd	44,750
Hg	27,780

So far as these data warrant us in drawing general conclusions, it appears that the quantity of heat produced during the occurrence of a similar chemical change increases as the atomic weight of the metal increases in the cases of even series members of Group II., but that the quantity of heat produced decreases as the atomic weight of the metals in odd series of the group increases. Further, it seems that the increase in the even series members is much less for equal increments of atomic weights than the decrease in the odd series members. And lastly it is seen that the value for magnesium, which is the first odd series member of the group, is generally nearly the same as the value for calcium, which is the first even series member for which thermal data have been observed. Unfortunately hardly any thermal measurements have yet been made for compounds of beryllium; the following numbers, taken from Thomsen's work, show that the heat of neutralisation of beryllium hydroxide is very much less than that of the other even series members of the group, or of magnesium, and approaches the values for zinc, cadmium, and mercury:—

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[1] The square bracket denotes that the thermal value of the chemical change which occurs between the bodies within the bracket is measured; the comma means that chemical action occurs between the bodies the symbols of which are separated by this comma; the symbols of elements and compounds are to be read in grams; the figures represent gram-units of heat produced; the symbol Aq is used to denote so large a mass of water that an increase in this mass would not affect the thermal value of the change. Thus $[Ca,Cl^2,Aq] = 187,600$ means that 187,600 gram-units of heat are produced when 40 grams of calcium and 71 grams of chlorine combine, in presence of much water, to produce 111 grams of calcium chloride.

[2] These figures represent the heats of formation of *solid* $HgCl_2$, Hg_2Cl_2, $HgBr_2$, Hg_2Br_2, HgI_2, and Hg_2I_2 respectively.

Q	[Q,2HClAq]
BeO_2H_2	16,100
CaO_2H_2	27,900
SrO_2H_2	27,630
BaO_2H_2	27,780
MgO_2H_2	27,690
ZnO_2H_2	19,880
CdO_2H_2	20,290
HgO	18,920

Looking at these thermal measurements as a whole it is clear that, thermally considered, magnesium is very analogous to the three metals Ca, Sr, and Ba; that the three metals Zn, Cd, and Hg form a second class, marked off from the Mg...Ba class; and that, if one may draw any conclusions from the meagre data, beryllium seems to belong to the zinc rather than to the magnesium class. A consideration of the thermal values of the reactions of the metals in Group II. with acids shows that mercury is more widely separated from the other members of the group than these other members are from one another. Thus, take the values of the differences (1) between the heats of formation of the chlorides of the metals and that of gaseous hydrochloric acid, and (2) between the heats of formation of aqueous solutions of the nitrates of the metals and that of aqueous nitric acid; these differences give comparative representations of the quantities of heat produced, or which disappear, when equivalent masses of the metals react (1) with the same (equivalent) mass of gaseous hydrochloric acid, and (2) with the same (equivalent) mass of nitric acid dissolved in much water:—

M	$[M,Cl^2]-[H^2,Cl^2]$	M	$[M,O^2,N^2O^4Aq]-[N^2O^5,Aq]$
Ca	125,820	Ca	117,520
Sr	140,550	Sr	125,770
Ba	150,740	Ba	127,380
Mg	107,010	Mg	116,840
Zn	53,210	Zn	42,870
Cd	49,240	Cd	26,360
Hg_2	18,600	Hg_2	−11,650 (used)
Hg	9,200	Hg	−22,570 (used)

As a general rule, such thermal data as are given here and elsewhere in this article represent differences between the quantities of energy degraded from more chemically available to less chemically available forms, during similar reactions. Of two systems producible from the same initial system, that one will be the more stable the production of which is attended with the running down of the greater quantity of energy. It is most important to trace connexions between the compositions of chemical systems and the quantities of energy degraded during the production of these systems; but such thermal data as are given here can only be regarded as affording bases for very rough comparisons of the stabilities of the various systems produced by the different chemical operations formulated (*v.* further EQUILIBRIUM, CHEMICAL; and PHYSICAL METHODS).

Further data on which comparisons of the compounds of the elements in Group II. may be based are furnished by (1) the melting-points, and (2) the so-called specific volumes, of similar compounds. The specific volume of a compound is defined as the quotient obtained by dividing the formula-weight by the specific gravity of the solid compound; it represents the volume, in cubic centimetres, occupied by the mass of the solid compound, in grams, represented by the formula of the compound. The difference between the specific volume of a binary compound and that of one of the elements contained in one formula-weight of the compound may be taken as representing the specific volume of the other element in one formula-weight of the compound; these differences afford useful data for comparing similar compounds of elements in the same or different groups:—

Melting-points of chlorides and bromides (approx.).

$BeCl_2$	600°	$BeBr_2$	600°
$CaCl_2$	720	$CaBr_2$	680
$SrCl_2$	825	$SrBr_2$	630
$BaCl_2$	800	$BaBr_2$	810
$MgCl_2$	700	$MgBr_2$	700
$ZnCl_2$	260	$ZnBr_2$	400
$CdCl_2$	540	$CdBr_2$	570
$HgCl_2$	280	$HgBr_2$	240

Spec. vols. of solid oxides MO.

	round numbers	differences
BeO	8	
CaO	18	 10
SrO	22	 4
BaO	28	 6
MgO	12	
ZnO	14	 2
CdO	16	 2
HgO	19	 8

Spec. vols. of MO—spec. vols. of M.
(= hypothetical spec. vols. of O in MO)

In BeO	+2·7
„ CaO	−7·2
„ SrO	−12·9
„ BaO	−8·5
„ MgO	−1·8
„ ZnO	+5·1
„ CdO	+5·5
„ HgO	+4·7

As regards the melting-points of chlorides and bromides, we see that the five metals Be, Ca, Sr, Ba, and Mg, are closely related to each other, while the three remaining metals of the group, viz. Zn, Cd, and Hg, form a class by themselves. As regards the specific volumes of oxides, we notice that the values increase from BeO to BaO, then fall to MgO, and again increase from MgO to HgO; the great difference between the value for CaO and that for BeO (10), and the smaller difference between the value for BeO and MgO (4), suggest that BeO is more allied to the group MgO . . . . . HgO than to the group CaO, SrO, BaO. An analogy between BeO and the oxides of Zn, Cd, and Hg, is also pointed to by the value for the specific volume of O in the oxides MO.

Finally, let us tabulate the differences between the values of the atomic weights of pairs of consecutive metals in the group we are considering:—

$$\textit{Even series}\ \left.\begin{matrix}\mathrm{Ca}-\mathrm{Be}\\ 40-9\end{matrix}\right\}=31\quad \left.\begin{matrix}\mathrm{Sr}-\mathrm{Ca}\\ 87-40\end{matrix}\right\}=47$$

$$\left.\begin{matrix}\mathrm{Ba}-\mathrm{Sr}\\ 137-87\end{matrix}\right\}=50;\ \frac{50+47}{2}=48{\cdot}5.$$

$$\textit{Odd series}\ \left.\begin{matrix}\mathrm{Zn}-\mathrm{Mg}\\ 65-24\end{matrix}\right\}=41\quad \left.\begin{matrix}\mathrm{Cd}-\mathrm{Zn}\\ 112-65\end{matrix}\right\}=47$$

$$\left.\begin{matrix}\mathrm{Hg}-\mathrm{Cd}\\ 200-112\end{matrix}\right\}=88=44\times 2;\ \frac{44+47+41}{3}=44.$$

$$\frac{47+50+41+47+44}{5}=45{\cdot}8.$$

Omitting the difference Ca-Be, it is seen that the difference between the atomic weights of a pair of consecutive elements approaches the value 45; and that the difference is rather larger in the cases of the elements belonging to even series than in those of elements belonging to odd series. But the difference Ca-Be is only 31: in this respect beryllium stands marked off from the other elements of the group. If the differences between the values of the atomic weights of the first and second even series members of Groups I. to VII. are tabulated, it is found that this difference varies from 32 (K-Li) to 36 (Mn-F), and has a mean value of 34; but 34 is considerably less than 45, which is about the mean difference between any two elements (omitting the elements from Li to Na) in the same group and in consecutive even, or consecutive odd, series.

Looking back at the properties of the elements in Group II., it appears that beryllium is distinctly marked off from the other elements of the group; that calcium, strontium, and barium are more closely related to each other than they are related to any other elements of the group; that the relations between zinc and cadmium are most marked; and that mercury is to some extent separated from the other members of the group. Beryllium approaches magnesium in the method of its preparation; in its high melting-point; in the unreadiness with which it oxidises; in the ease with which its hydroxide is decomposed by heat; in the solubility of its sulphate; in the specific volume of its oxide; and in some other properties. Beryllium approaches calcium, among other respects, in the nature of its spectrum; and in the readiness with which its hydroxide combines with carbon dioxide. In the melting-point of its chloride and bromide, beryllium approaches the three metals calcium, strontium, and barium. The analogies between beryllium and zinc are marked by the following among other properties: action on water; solubility in aqueous potash; crystalline form of the oxides. The solubility of beryllium sulphate in water; the readiness with which basic salts, and also double salts, of beryllium are produced; the existence of gasifiable chloride, bromide, ethide, and propide, of beryllium; the specific volume of oxygen in beryllium oxide; and the thermal value of the neutralisation, by aqueous hydrochloric acid, of beryllium hydroxide; these properties indicate the analogy between beryllium and the three odd series members of the group, zinc, cadmium, and mercury. Calcium, strontium, and barium certainly stand by themselves; but in the specific volume of the oxygen in its oxide, and more especially in the thermal values of similar reactions, the odd series metal magnesium is closely related to these three even series metals. Mercury is marked off from the other elements of the group by the fact that it forms two series of salts, and by the thermal values of the reactions between it and hydrochloric and nitric acids; but in the general character of its persalts, in the melting-points of its chloride and bromide, in the specific volume of its oxide and of the oxygen therein, mercury is clearly related to zinc and cadmium; and in the solubility of its oxide in molten potash, the relationship of mercury more especially to zinc and beryllium is rendered evident. An element has yet to be discovered which shall have an atomic weight equal to about 158, and which shall form a link between cadmium and zinc on one side and mercury on the other.

Putting together all we have learned of the elements and the compounds of the elements in Group II., we see that the group contains certain sub-groups or families, but that the special characteristics of these families are balanced by the strength of the group-character which impresses itself on all the members of the group.

Group VI. comprises the following elements:—

Even series

2	4	6	8	10	12
O = 16	Cr = 52	Mo = 96	—	W = 181	U = 240

Odd series

3	5	7	9	11
S = 32	Se = 79	Te = 125	—	—

We have here two families: the even series members O, Cr, Mo, W, and U; and the odd series members S, Se, and Te. But in many respects the first member of the even series family, oxygen, more resembles the odd series family than it resembles the other members of its own family. There is a distinct line of separation between oxygen on one side and Cr, Mo, W, and U on the other side. The four members of the even series family Cr . . . . U may be divided into two sub-families, Cr and Mo, and W and U; but there are well-marked analogies between Cr and U on the one hand, and between Mo and W on the other hand. Finally, some of the members of the even series family, besides oxygen, show very distinct relations to members of the odd series family; *e.g.* Cr and S, and U and Te, are more or less closely related.

Let us consider these relationships very briefly. The compositions of the binary compounds of O, S, Se, and Te, emphasise the relations between the four elements: we have MH_2, MCl_2, MK_2, MCa, $M(C_nH_{2n+1})_2$, &c., where M = O, S, Se, or Te. The properties of these compounds are also very similar. No hydrides of the other even series members (Cr . . . . U) are known, the best-marked chlorides of these elements are not MCl_2, nor do these elements form compounds with K, Ca, or the radicles C_nH_{2n+1}. There is a less-marked gap between the physical properties of O on one hand, and S, Se, and Te on the other, than between the former element and Cr, Mo, W, and U: thus, the melting-points of S, Se, and Te all lie under 550°, whereas Cr, Mo, and W, are scarcely fusible at the highest attainable temperatures, and U melts only at a full red heat. The specific gravities also of S and Se are less than 5, whereas the values of this quantity for Cr . . . . U vary from 6·7 (Cr) to 19 (W). The specific gravity of Te is about

6·2. The elements S, Se, and Te, are distinctly non-metallic and negative; their oxides are acid-forming; these elements do not replace the hydrogen of acids with formation of salts; in these respects they approach closely to oxygen, which is the typical non-metallic acid-forming element. Tellurium, however, is to some extent separated from selenion and sulphur; it is a white, brittle solid; its haloid compounds are much more stable than those of S or Se; its oxides are not strongly acid-forming; the acids H_2TeO_3 and H_2TeO_4 are easily separated into water and anhydride, they are only slightly soluble in water, and are feeble acids (this statement may be made although the *relative affinities* of these acids have not yet been determined). Thomsen's measurements of the relative affinities of sulphuric and selenic acids (H_2SO_4 and H_2SeO_4), and the confirmation of these results by Ostwald's study of the electrical conductivities of aqueous solutions of these acids with varying masses of water (*v.* AFFINITY, vol. i. pp. 75, 81, 83), show that these two acids are most closely related in their powers of combining with bases. The heat of formation of aqueous solutions of the oxides MO_3, however, point to a closer relation between Se and Te on one hand, than between either of these elements and S on the other hand: thus,

$$[M, O^3, Aq] = \begin{cases} 142{,}410 \text{ when } M = S \\ 76{,}660 \quad ,, \quad M = Se \\ 98{,}380 \quad ,, \quad M = Te. \end{cases}$$

Notwithstanding these resemblances we must admit that oxygen is distinctly cut off from the other members of the group, whether they be even series, or odd series, elements. Thus the thermal values of the formation of hydrides reveal a great gap between O and S: $[H^2, O] = 68{,}360$, but $[H^2, S] = 4{,}710$ (unfortunately values for $[H^2, Se]$ and $[H^2, Te]$ have not yet been determined). Oxygen, like beryllium in Group II., is a so-called 'typical' element; the relations of this element to the odd series family of its group—S, Se, and Te—are not unlike the relations of the typical Be to the members of its group which belong to odd series Mg, Zn, Cd. Oxygen is distinctly cut off from the even family Cr . . . . U by its physical properties; by the composition of compounds with the same elements, *e.g.* OCl_2, O_2Cl, $CrCl_3$, $MOCl_5$, WCl_6, UCl_4; by the properties of many of these compounds, *e.g.* OCl_2 boils at - 18°, $MOCl_5$ and WCl_6 melt between 200° and 300°, the heat of formation of OCl_2 has a large negative value, the heats of formation of chlorides of the other elements have not been determined, but from established analogies there can be no doubt that the numbers representing these heats of formation have large positive values; further the elements Cr, Mo, W, U, act both as acid-forming and salt-forming elements, whereas oxygen is in the most marked way the typical acid-forming element.

The even family Cr . . . . U may be broadly divided into two sub-families, Cr and Mo, and W and U. Thus the specific gravities of Cr and Mo are, respectively, 6·7 and 8·5, of W and U 19 and 18·5; the specific volumes (*i.e.* atomic weight ÷ S.G. of solid) are 7·7 and 11·3, and 9·7 and 12·9. Some of the oxides of chromium, *e.g.* Cr_2O_3, are distinctly salt-forming, but CrO_3 is the anhydride of a well-marked acid, H_2CrO_4, from which is derived a large series of well-marked salts, for the most part isomorphous with similar sulphates and manganates. The oxides of Mo can scarcely be classed as salt-forming, although MoO_2 is said to dissolve in acids without evolution of oxygen; MoO_3 is the anhydride of an acid H_2MoO_4; two classes of chromium salts exist, chromous salts represented by $CrSO_4 7H_2O$, and the more stable chromic salts represented by $Cr_2 3SO_4$, $Cr_2 6NO_3$, &c.; hydrated oxides of the composition $MO.xH_2O$, both of Cr and Mo, seem to exist, but they are easily oxidised to compounds of the form $M_2O_3.xH_2O$. The relations of W to U are similar to those of Mo to Cr; few, if any, distinct salts are known obtained by the replacement of the hydrogen of acids by W, but U forms two well-marked series of salts, represented by USO_4 and UO_2SO_4 respectively; the oxides WO_3 and UO_3 are both anhydrides of acids $H_2W(U)O_4$. The oxide WO_2 resembles MoO_2 in that it dissolves in acids without evolution of oxygen; WO_3 and MoO_3 also form double compounds with various anhydrides, *e.g.* with P_2O_5, SO_3, &c. The salt-forming character of the oxides of the family Cr, Mo, W, U, decreases from Cr to Mo, and again increases from W to U, but at the same time the extremes of the family (Cr and U) produce more distinctly marked acid-forming oxides (MO_3) than either of the means (Mo and W). Finally, the highest members of the odd and even series of Group VI., Te and U, are, on the whole, more positive (although U produces a well-marked acid-forming oxide) than the other members of either family; and the first member of the even family, viz. Cr (excepting oxygen, which belongs both to the odd and the even families), shows fairly marked analogies with the first member of the odd family, viz. S.

Summing up the characteristics of Group VI., and comparing them with those of Group II., we see that the former group, as a whole, is non-metallic; its members are comparatively negative, and their best-marked oxides, as a class, are acid-forming; but we find in it two families, one of which, Cr . . . U, is more metallic and salt-forming, and the other, S . . . Te, is more non-metallic and acid-forming. Similarly we find in Group II. two families, one more distinctly metallic than the other; but, on the other hand, the whole character of Group II. is metallic, and the oxides of the members of the group are salt-forming. In each group we have found a 'typical' element: in Group VI. oxygen, in Group II. beryllium; the properties of this element to some extent summarise the properties of all the members of the group. The difference between the value of the atomic weight of oxygen and that of the next even series member of Group VI., viz. Cr, is 36; the difference between the atomic weight of beryllium and that of the next even series member of Group II., viz. Ca, is 31; the mean difference between any two consecutive even or odd members of either group is about 45; oxygen perhaps rather more closely approaches the properties of the odd family of its group than beryllium approaches the properties of the family of Group II. the members of which belong to odd series.

Let us now turn for a moment to those groups in which the family-character preponderates over the group-character, Groups I. and VII., and to those in which the group-character is much more marked than the family-character, Groups III., IV., and V.

Group I.

Even Series—

2	4	6	8
Li = 7	K = 39	Rb = 85	Cs = 133

Odd Series—

3	5	7	9	11
Na = 23	Cu = 63	Ag = 108	—	Au = 197

The very marked similarity between Li, Na, K, Rb, and Cs, both as regards the metals themselves and their compounds, quite overshadows the much more feebly marked similarities which exist between Cu, Ag, and Au. But the thermal values of the reactions between lithium and water, between Li and O, Li and Cl, or Li and Br in presence of water, &c., the comparative insolubility of LiOH, Li_2CO_3, Li_3PO_4, the non-formation of an alum containing Li, the non-formation of double salts containing LiCl, the comparatively less ready oxidation of Li, and some other properties, show that lithium is to some extent separated from the metals Na . . . Cs. The properties of those salts of copper of which the chloride Cu_2Cl_2 is a representative, exhibit some analogies with those of the compounds of lithium. Silver approaches the even family of Group I. in the composition of all its well-marked salts, in the distinct alkalinity of its oxide, and in the fact that silver sulphate forms an alum. Although gold is distinctly marked off from the other members of the group, yet in the softness of the metal, in the facts that compounds of the form M_2O are known, that the auric haloid compounds very easily form double salts with the haloid compounds of Na . . . Cs, that Au_2O and Au_2S are sol. in water, and in a few other respects, this metal exhibits some analogies with the even family of the group and with sodium.

Group VII.

Even Series—

2	4
F = 19	Mn = 55

Odd Series—

3	5	7
Cl = 35·5	Br = 80	I = 127

Here the family-character of the odd series members impresses itself on the whole group; fluorine exhibits definite relations to the odd family, but the two facts that it forms no compounds with oxygen, and that its compounds with hydrogen and the alkali metals exhibit the greatest readiness to form double salts, suffice to cut it off to some extent from Cl, Br, and I. The heat of neutralisation of HF is considerably larger than the heat of neutralisation of HCl or HBr; [HMAq, NaOHAq] = 13,740 when M = Cl or Br, but = 16,250 when M = F, but the ***relative affinity*** of HF is very small; it is approximately equal to 5 when that of HCl = 100, and that of HBr = 95 or so. The thermal values of some similar reactions of Cl, Br, and I, show that these elements are not so closely related to each other as a consideration of the outstanding chemical properties of their compounds would lead one to suppose; thus, [H, Cl] = 22,000; [H, Br] = 8,010; [H, I] = −6,040 (absorbed). The differences between the properties of perchloric and periodic acids also emphasise the differences between chlorine and iodine. The isomorphism of permanganates and perchlorates, the markedly acid-forming character of MnO_2, and the existence of permanganic acid, establish a connection, feeble though it be, between manganese and the other members of Group VII. In studying the relations of the members of this group it should not be forgotten that no representative of series 6, 8, 9, 10, 11, 12 or 13, is at present known.

Group III.

Even Series—

2	4	6	8	10
B = 11	Sc = 44	Y = 89	La = 139	Yb = 173

Odd Series—

3	5	7	9	11
•Al = 27	Ga = 69	In = 114	—	Tl = 204

The group-character is here impressed on all the elements; Al and Ga form a family to which In is allied and Tl shows analogies in one class of compounds; Sc is not without analogies to Al and Ga, it is also distinctly related to B; of the other metals too little is known to enable us clearly to see their analogies. The last member of the group, thallium, astonishes us by the marked way in which in the thallous salts (Tl_2O, Tl_2SO_4, &c.) it approaches the even series members of Group I., viz. Li . . . Cs. The typical element, boron, while showing analogies with all the other members of the group, and with other elements, *e.g.* with C and Si, is yet different from any of them; it is a good representative of the want of family likeness between the even series members or the odd series members of this group, and at the same time of the distinctly group character which is impressed on all the elements in the group.

Group IV.

Even Series—

2	4	6	8	10	12
C = 12	Ti = 28	Zr = 90	Ce = 140	—	Th = 232

Odd Series—

3	5	7	9	11
Si = 28	Ge = 72	Sn = 118	—	Pb = 207

Here again the even series members do not form a family marked off from the odd series members. Certain minor families are, it is true, to be found in the group, but on the whole the group-character much preponderates. Carbon stands by itself; it is marked off from all other elements by the immense number and complexity of the compounds which it forms with H, O, N, S, and the halogens. Most nearly related to carbon we have the first odd series member of the group, silicon; the silico-organic compounds, the existence of allotropic varieties of silicon, the relations between the specific heat of silicon and temperature, the thermal values of similar reactions of carbon and silicon, exhibit the analogy between these elements (*v.* CARBON GROUP OF ELEMENTS). The physical properties of Ti and Zr, the stability, and acid-forming character, of their oxides MO_2, the volatility of their chlorides MCl_4, the isomorphism of some titanates and zirconates with silicates, these points emphasise the connections between Ti, Zr, Si, and **C**. But the formation of the sulphate $Ti(SO_4)_2$, of various salts of zirconium, *e.g.* $Zr(SO_4)_2$, $Zr(NO_3)_4$, &c., show that these elements incline also towards Ce and Th which follow them in the even series, and towards Sn and Pb which belong to odd series of the same group. Cerium forms salts analogous to those of zirconium, *e.g.* $Ce(SO_4)_2$, but its most marked compounds are represented by the peroxide CeO_2. Thorium again approaches more closely to Ti and Zr than Ce does; the existence of ThO_2, $Th(SO_4)_2$, K_2ThF_6, ThF_4, marks this analogy. Tin and lead resemble each other physically more than they resemble other members of the group; they exhibit the group-character in their oxides MO and MO_2, in their chlorides (or ethides) MCl_4, in their salts K_2MO_3; tin further exhibits this character in its stannic salts $Sn(SO_4)_2$, $Sn(NO_3)_4$, &c.; but each of these elements produces compounds which have no analogies among those of the other members of the group.

Group V.

Even Series—

2	4	6	8	10
N=14	V=51	Nb=94	Di=144	Ta=182

Odd Series—

3	5	7	9	11
P=31	As=75	Sb=120	Er=166	Bi=208

The group-character is so impressed upon the whole of these elements that we may almost say there are no families; and yet the group falls into two subdivisions, each of which nearly repeats the characteristics of the other. From N to Ta we pass from a most markedly non-metallic, acid-forming, element to an element which, on the whole, is more metallic than non-metallic; from P to Bi we repeat the same gradation, only here the starting-point is an element rather less negative in its functions than nitrogen, and the last member of the series is decidedly more positive than tantalum. The less prominently acid-forming character of phosphorus as compared with that of nitrogen is exhibited, among other ways, by the *relative affinities* of nitric and phosphoric acids; the former being taken as 100, the latter is approximately equal to 20. The balance of metallic and non-metallic properties in tantalum is well shewn by the action of acids on aqueous solutions of potassium tantalate. Acids whose relative affinity is large, *e.g.* sulphuric or hydrochloric acids (affinity = (approx.) 70 and 100), decompose this salt and pp. tantalic acid (H_3TaO_4) in combination with a portion of the acid used; acids with a smaller affinity, *e.g.* sulphurous acid (affinity not determined, but, from Ostwald's electrical experiments, it must be considerably less than H_2SO_4), completely pp. pure tantalic acid; acids with yet smaller affinities, *e.g.* H_3PO_4 (affinity about 20), pp. potassium tantalate; and, lastly, acids with very small affinities, *e.g.* acetic or succinic acid (affinities 6 and 7 respectively), cause no pp. when added to solutions of potassium tantalate. That the last member of the odd series family, viz. bismuth, is more metallic than the last member of the even series family, viz. tantalum, is shown by the fact that in all its well-established compounds bismuth is positive to the other elements with which it is combined, and that if hydrated bismuthic oxide, $Bi_2O_5xH_2O$, acts as an acid it forms salts which can scarcely be obtained in definite form, and which are certainly at least partly decomposed by the action of hot water.

We have thus endeavoured to draw the outlines of a scheme of classification of the elements and their compounds based on the comparison of those which are similar in physical and chemical properties, and by similar chemical properties we have implied similarity of function and similarity of composition. It yet remains, however, to examine somewhat more closely into the composition of the compounds classified, with the view of finding whether anything can be learnt of the structure of these bodies in the sense which is given to the word structure by the molecular and atomic theory. The compositions of the highest oxides, and of some of the other compounds of the elements, appear to vary periodically with variations in the atomic weights of the elements. If R represent the mass of an element expressed by its atomic weight, and if X represent the masses of F, Cl, Br, or I, expressed by the respective atomic weights of these elements, or the masses of the groups OH, NO_3, ClO_4, &c., expressed by these formulæ, or the masses of the elements or groups of elements expressed by *halves* of the formulæ O, S, SO_4, CrO_4, &c., then we may say that the compositions of the oxides

$$R_2O,\ RO,\ R_2O_3,\ RO_2,\ R_2O_5,$$

are expressed by the symbols

$$RX,\ RX_2,\ RX_3,\ RX_4,\ RX_5.$$

We may also say that the compositions of the salts

$$R_2SO_4;\ R(NO_3)_2;\ R(NO_3)_3,\ ROCl,\ R_2(SO_4)_3,\ RONO_3;\ ROCl_3,$$

are expressed by the symbols

$$RX;\ RX_2;\ RX_3,\ RX_3,\ RX_4,\ RX_4;\ RX_5.$$

In this way it becomes possible to give general expressions for the forms of the highest stable oxides characteristic of each group, and also for the forms of the highest well-marked salts of the elements of each group. It is generally found that the greater the value of X in the oxide-form the smaller is the value of X in the salt-form. The following symbols are given by Brauner (*Sitz. W.* [*Math.-naturwiss. Classe*], 84, 1165):—

Groups .	. **I.**	**II.**	**III.**	**IV.**
Oxide forms	. RX	RX_2	RX_3	RX_4
Salt forms	. RX_7	RX_6	RX_5	RX_4
Groups .	. **V.**	**VI.**	**VII.**	**VIII.**
Oxide forms	. RX_5	RX_6	RX_7	RX_8
Salt forms	. RX_3	RX_2	RX	R_2X

The characteristic oxides of most of the elements belonging to Group I., Li . . . . Au, are represented by the general symbol R_2O; putting $X = \frac{O}{2}$, the ratio of metal to O in these oxides is expressed by the symbol RX. Similarly the composition of the characteristic oxides of the elements of Group II., Be . . . . Hg, is represented by RO; but, as $O = X_2$, the symbol RX_2 expresses the same composition as the symbol RO. The salt-forms, RX_7 . . . . RX, are interpreted in the same way as the oxide-forms. Thus Na forms a hydrated hydroxide of the composition Na.OH.3H(OH); now, if X = H = OH, this compound belongs to the general form RX_7; similarly, the salt S_2Cl_2 (Group VI.) belongs to the general form RX. These symbols must be interpreted only in a wide and general way. For instance, the highest oxide of a metal of Group I. is K_2O_4, and this belongs to the form RX_4, but the most characteristic oxides (M_2O) of the majority of the metals of this group belong to the form RX; the most characteristic oxide of copper, however, is CuO, and of gold is Au_2O_3; these oxides belong, respectively, to the forms RX_2 and RX_3. But Cu and Au are classed both in Groups I. and VIII.; the oxide form of Group VIII. is RX_8, and the salt form is R_2X; but no well-marked oxide or salt of either Cu or Au belongs to either of these forms. So again, Group V. has assigned to it the oxide form RX_5 and the salt form RX_3; the oxides N_2O_5 . . . . Bi_2O_5 certainly belong to the form RX_5; the salts $NO_2(OH)$, $PO_2(OH)$, &c., belong to the form RX_3; but the salts $PO(OH)_3$, $Sb_2O_3(OH)_4$, &c., belong to the form RX_5, and the salt $Bi_2O_5H(OH)$ to the form RX_6. The symbols given must then be interpreted as representing the limits between which the compositions of most of the compounds of each group vary; that with the greater value of X represents the composition of the highest compounds, and that with the smaller value of X represents the composition of the lowest compounds of the elements in any specified group. The expressions 'salt-forms' and 'oxide-forms' are not to be recommended; it would be better to summarise the facts of composition in some such way as this:—

Limiting forms between which the composition of compounds varies.

Groups.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
RX_7 to RX	RX_6 to RX_2	RX_5 to RX_3	RX_4	RX_5 to RX_3	RX_6 to RX_2	RX_7 to RX	RX_8 to R_2X

In Groups I. to III. the lower form usually represents the composition of what may be called the typical group oxides; in Groups V. to VIII. the higher form usually represents the composition of the typical group oxides. The 'typical group oxides' are not always the most stable oxides; *e.g.* $Bi_2O_5(RX_5)$ is less stable than $Bi_2O_3(RX_3)$ (Group V.), $PbO_2(RX_4)$ is less stable than $PbO(RX_2)$ (Group IV.). Sometimes these 'typical group oxides' are scarcely known to exist; *e.g.* no oxide of the form RX_7 has certainly been obtained where R is an element of Group VII.; but the composition of the highest, and speaking broadly the most stable, acids (? acids with largest affinities) of this group of acid-forming elements is represented by the symbol HMO_4 (where M = Cl, I, or Mn), and the hypothetical anhydrides of these acids have the composition M_2O_7, that is, are represented by the symbol RX_7. Of the 11 elements which ought to find places in Group VII., only 5 are actually known; when the remaining 6 have been prepared and their compounds examined some of them may be found to form oxides belonging to the form RX_7. Concerning Group VIII., it is difficult to say which oxides of the members of this group are to be taken as the typical group oxides; for Ni, Co, and Cu, one would be inclined to adopt the oxides $MO(RX_2)$, for Fe and Au the oxides $M_2O_3(RX_3)$, for silver the oxide $Ag_2O(RX)$, and for Os and Ru the oxides $MO_4(RX_8)$. The compositions of these vary between the limiting forms RX_8 and RX; there is probably a suboxide of silver (Ag_4O) belonging to the form R_2X.

When we deal with compounds other than oxides, the application of the limiting forms becomes yet more difficult. If the term salt be taken to mean (1) acids, in the cases of markedly negative elements, or (2) metallic derivatives of acids, in the cases of markedly positive elements, then the characteristic salts of the elements of Group I. are represented by Li_2SO_4, and they belong to the form RX; the characteristic salts of Group II. are represented by $BeSO_4$, and they belong to the form RX_2. Tabulating in this way the characteristic salts and their general symbols for the groups, we have the following result:—

Groups	I.	II.	III.	IV.
Salt .	Li_2SO_4	$BeSO_4$	Al_23SO_4, $B(OH)_3$	CCl_4, $Sn(SO_4)_2$
Form .	RX	RX_2	RX_3	RX_4

Group	V.		
Salt . .	$NO_2(OH)$, $Bi3NO_3$	and	$PO(OH)_3$, $SbCl_5$
Form . .	RX_3		RX_5

Group	VI.				
Salt	Cr_23SO_4	and	UCl_4, $U(SO_4)_2$	and	WCl_6, $SO_2(OH)_2$
Form	RX_3		RX_4		RX_6

Group	VII.		
Salt . . .	$MnSO_4$	and	$MnO_3(OH)$, $ClO_3(OH)$
Form . . .	RX_2		RX_7

Group	VIII.						
Salt .	$FeSO_4$	and	Fe_23SO_4, $AuO(OK)$	and	$PtCl_4$	and	$OsO(OK)H(OH)$
Form ,	RX_2		RX_3		RX_4		RX_8
		and	$PtClSO_2(OH)$, $PtPCl_5$, $PtO_22H(OH)$				
			RX_6				

If the term salt is used to include all compounds of a given element, whether these be classed as double salts, basic salts, hydroxides, &c., &c., then it is easy to find representatives of most forms, intermediate between the limiting group forms, for the members of any group. For instance, salts higher than RX and up to RX_7 belonging to Group I. are represented by KI_3 (RX_4), $KAuCl_4$ and $KAuBr_4$ (RX_5), and Na(OH).3H(OH) (RX_7); salts of the form RX_5 belonging to Group III. are represented by $BOCl_3$, $AlKCl_4$, and $AlKI_4$; salts belonging to Group II., of the form RX_4, are represented by $MgNaF_3$ and $BeKF_3$, and of the form RX_6 by BeK_2F_4, ZnK_2F_4, and $BaO_2H(OH)$. It has been sought to trace special relations between the forms of hydrides and hydrated oxides in each group; thus, Mendelejeff gives the following symbols:—

Groups	I.	II.	III.
Hydride form	RH_7	RH_6	RH_5
Example	—	—	—
Hydrated oxide form	RH_7O_4	RH_6O_4	RH_5O_4
Example	NaOH.3HOH	$Ca(OH)_2.2HOH$	$\frac{Al_2O_3.5H_2O}{2}$

Groups	IV.	V.	VI.	VII.
Hydride form	RH_4	RH_3	RH_2	RH
Example	CH_4	PH_3	OH_2	ClH
Hydrated oxide form	RH_4O_4	RH_3O_4	RH_2O_4	RHO_4
Example	$Si(OH)_4$	$PO(OH)_3$	$SO_2(OH)_2$	$ClO_3(OH)$

The limiting forms of compounds which the periodic law supplies as an aid in classifying elements and compounds are undoubtedly useful if employed with caution. The search for such limiting forms has always been carried on in chemistry. Dalton and Berzelius made it the main business of their lives, as chemists, to seek for formulæ which should express the maximum numbers of atoms of each element capable of combining together. Berzelius developed his all-embracing system of dualism on the conception that every compound is built up of two parts, themselves either simple or complex, one of which is electrically positive towards the other (*v.* DUALISM). This conception at once led to that of radicles, or groups of atoms which remain so closely united throughout various chemical changes that the functions performed by them in these changes are, to all intents, the functions of single atoms. The conception of the radicle brought with it into chemistry a mode of reasoning which has been of much importance in the advances made within recent years. The group of atoms named a radicle was not known, as a rule, except as it manifested itself in the reactions of compounds supposed to be formed by the union of the radicle with other radicles or with elements. The arguments for or against an explanation of a chemical occurrence wherein radicles were regarded as taking part were necessarily based on experimental evidence which failed to bring into court the actual complex of atoms asserted to be an essential part of the mechanism of the change. Chemists became accustomed to think of certain collocations of atoms as necessary factors in this or that operation; but they attributed actual existence to these atomic groups only when mutual action and reaction was occurring between them and other groups, or single atoms. The way was thus prepared for regarding all chemical phenomena as essentially the results of mutual actions and reactions between elements or compounds, and for the conception of chemistry as the study, not so much of this kind of homogeneous matter, or that, as of the connections between the changes of composition and the changes of properties which these kinds of matters exhibit when they mutually act and react under defined conditions. The conception of radicles went hand in hand with that of types. The meaning of a typical classification of elements and compounds has been illustrated in the present article (*v.* also RADICLES and TYPES). The most complete outcome of this method is the classification based upon the periodic law; and the use of typical forms to express the compositions of oxides, and other compounds, of each group of elements, is one of the points wherein the periodic law emphasises the continuity of chemical science.

The great objection to the use of these typical or limiting forms seems to be that they are based too exclusively on the notion of showing the composition of compounds, and that their employment tends to hide the importance of combining the study of composition with that of properties. The purely empirical compositions of the salts $KAuCl_4$ and $NaOH.3H_2O$ are certainly represented by the symbols RX_5 and RX_7, as illustrations of the existence of which forms in Group I. the salts in question are brought forward; but a comparison of the properties of these salts with those of such compounds as Au_2O_3 and Na_2O at once shows that there is a great difference between the two classes of compounds. The mere fact that platinum forms a compound which, by the dexterous use of symbols, may be represented as belonging to the type RX_8, can be of little assistance in developing a rational scheme of classification. One of the platinum compounds of this type is $PtClSO_2(OH)$; why should not this compound be used to prove that sulphur forms compounds of the type RX_8, or that chlorine forms compounds of the type RX_8? Why is the compound BeK_2F_4 (*i.e.* $BeF_2.2KF$) to be adduced as an example of the existence of compounds of the form RX_6 in Group II., and not as an example of the existence of compounds of the form RX_3 in Group I., or of the form RX in Group VII.? If empirical composition is everything, it is only necessary to write this double fluoride as K_2BeF_4, to prove that it belongs to the ($R_2X_2X_4$ that is) RX_3 form of Group I.; or as F_4BeK_2, to prove that it is an example of the ($R_4X_2X_2$ that is) RX form in Group VII.

The history of the classifications which at different times have been founded on the notion of types conclusively proves that unless attention is constantly paid to the functions, as well as to the compositions, of the bodies classified, the systems do little to further chemical advance, and the conception on which they are founded is shorn of most of its value as a science-producing idea. It is most certainly true that the classification presented by the periodic law is based on the study at once of the compositions and the functions of the bodies classified; it is this, indeed, which gives the method so marked an advantage over all others; but just because of this fact should we be ever on our guard against placing too much trust in any single part of the method, unless that part is used in conjunction with the other parts, all of which together constitute the complete method.

The forms assigned to many salts, especially to the double and basic salts, almost wholly depend on the values given to the different elementary atoms. Why do we begin by asserting that $X = F, Cl, Br, I, NO_3, ClO_3, \frac{SO_4}{2}, \frac{PO_4}{3}, \frac{O}{2}$, &c.? How is the equivalency assumed to exist between these atoms and groups of atoms actually proved to exist? In writing the equations $F = Cl = Br = NO_3 = \frac{O}{2} = \frac{SO_4}{2}$, and in applying these to the study of typical forms of salts, we are making many far-reaching assumptions. The chief assumptions are two. In the first place, the molecular theory is carried over from gases and applied without modification to liquids and solids. In the second place the tentative hypotheses which chemists have framed to help them to group together what they have learned from the study of gaseous compounds regarding the equivalency of atoms are applied to solid and liquid compounds. Both assumptions are made without acknowledging the great differences between the phenomena on which a theory of the structure of liquids and solids must rest, and the phenomena from which the prevailing theory of the structure of gases has been developed. The very word molecule is defined only in terms of gaseous phenomena. It is the study of gaseous phenomena that has obliged chemists to recognise two orders of small particles, the molecule and the atom; and it is from the study of the mutual actions of gases that a working hypothesis of the structure of molecules has been developed. In the article ATOMIC AND MOLECULAR WEIGHTS (vol. i. p. 319), an attempt has been made to show that the reacting chemical unit of a compound should at present be regarded as a collocation of atoms, which, under definite conditions, takes part in chemical changes as an individual existence. Admitting the existence of such collocations of atoms, it follows almost necessarily from every-day chemical facts that the groups have definite configurations, which remain unchanged throughout considerable changes of conditions; for all the facts of chemical change force us to regard most chemical properties as dependent on the relative arrangement, as well as on the nature and number, of the atoms which form the reacting units of compounds. There are few, if any, properties of bodies which, like weight, are the sums of the properties of the atoms, and, like the volumes occupied by gaseous compounds on the other hand, are dependent only on the state of combination of the atoms. But while we admit that the chemical properties of liquid and solid compounds are partly conditioned by the configuration of the atoms which constitute their reacting units, we cannot admit, on present evidence, that these configurations do not undergo considerable changes under the influence of other kinds of matter, or of physical agencies. We rather assert that what we know of these collocations of atoms (and what we know is as nothing compared with what we do not know) favours the view that their structure is easily changed, and that in this respect they present gradations from those which are so chemically mobile as scarcely to be recognised as definite chemical individuals, to those which are so chemically stable as almost to merit the name of molecules. If then we refuse to speculate regarding the structure of the atomic groups which seem to form the reacting units of liquid and solid compounds; and if, as a consequence of this, we also refuse to admit the validity of any arrangement of the atoms of solid and liquid compounds in order of strict equivalency—for equivalency means equal value in exchange, and the chemical equivalency of atoms can only be known when we know the functions performed by the various atoms in molecules of similar structure—can we hope to learn anything definite regarding the equivalencies of the atoms which constitute the molecules of gaseous compounds?

The subject of the equivalency of atoms goes hand in hand with that of the structure of molecules. The subject is too large to be discussed in an article on classification; but it is necessary to sketch the outlines of it as sharply as possible. All gaseous molecules formed by the union of atoms of *hydrogen*, *fluorine*, *chlorine*, *bromine*, and *iodine* are formed of two atoms; the molecules in question are these: H_2, Cl_2, Br_2, I_2, HF, HCl, HBr, HI (at very high temperatures the molecule of iodine is monatomic).

Those atoms which combine each with a single other atom to form a gaseous molecule are called monovalent atoms; the standard monovalent atoms are H, F, Cl, Br, and I. If the gaseous molecules formed by the union of atoms of H, F, Cl, Br, or I, with other atoms are tabulated, and the other atoms are then arranged in classes according as they are each found to combine with one, two, &c. atoms of H, F, Cl, Br, or I, the following arrangement results (*v.* next page). The atoms in column I. are monovalent; the atoms in column II. are called divalent, those in column III. trivalent, and so on. Atoms whose valencies are greater than one may be classed together as polyvalent. Of the 39 elements (exclusive of the 5 standard monovalent atoms) in these six columns, at least five occur each in two columns, viz. Hg, In, P, Sn, W (In probably occurs in three columns); the atoms of Ga, Cr, and Fe are probably also both divalent and trivalent.

The valency or equivalency (or quantivalence) of an elementary atom may be defined as *the number which expresses the maximum number of*

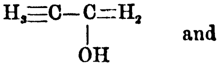
Monovalent atoms H, F, Cl, Br, I.

Atoms which produce compound gaseous molecules by union each with

I. *one monovalent atom*	II. *two monovalent atoms*	III. *three monovalent atoms*	IV. *four monovalent atoms*	V. *five monovalent atoms*	VI. *six monovalent atoms*
K, Rb, Cs, Hg, Ag, Tl, (?In).	O, S, Se, Te, Be, Cd, Zn, Hg, Sn, Pb, Mn, In, (?Ga, Cr, Fe).	B, N, P, As, Sb, Bi, In, Cr, Fe, Al, Ga.	C, Si, Ti, Ge, Zr, V, Sn, Th, U.	P, Nb, Ta, Mo, W.	W.

monovalent atoms (i.e. *atoms of* H, F, Cl, Br, *or* I) *with which the given atom is found to combine to form a gaseous molecule.* When bismuth combines with chlorine to form bismuthous chloride, one atom of the metal combines with three atoms of the halogen, and the molecule $BiCl_3$ is produced. When hydrogen combines with chlorine to form hydrochloric acid, one atom of hydrogen combines with one atom of the halogen and the molecule HCl is produced. As a single atom of Bi combines with three times as many atoms of chlorine as an atom of hydrogen combines with, an atom of bismuth is said to be equivalent to three atoms of hydrogen. In the molecule formed by the union of atoms of H and Cl, viz. HCl, there must be direct mutual action and reaction between the two atoms; in the molecule formed by the union of atoms of Bi and Cl, viz. $BiCl_3$, there may or may not be direct mutual action between the Bi atom and each of the Cl atoms. But the atom of chlorine is monovalent (*i.e.* combines with a single other atom to form a molecule), by definition, and by reason of the facts on which the definition is based; the hypothesis most in keeping with the monovalency of the chlorine atom is that each atom of chlorine in the molecule $BiCl_3$ directly acts on, and is acted on by, the atom of bismuth. Similarly, because of the existence of the molecule $SbCl_3$, the atom of Sb is said to be equivalent to three atoms of hydrogen; and, further, one atom of Sb is said to be equivalent to one atom of Bi. The conception of equivalency is here evidently that of equal value in exchange. One atom of Bi can be exchanged for one atom of Sb; one atom of O can be exchanged for one atom of Se; one atom of C can be exchanged for one atom of Si; one atom of Mo can be exchanged for one atom of W; and in each case the other parts of the molecules between which the exchange is effected remain unchanged. (The molecules in question are: $BiCl_3$ and $SbCl_3$; OH_2 and SeH_2; CCl_4 and $SiCl_4$; $MoCl_5$ and WCl_5.) The molecules concerned in the various transactions may be said, without putting too great a strain on the words, to have similar structures. But the notion of equivalency is carried further; an atom of N cannot be exchanged for an atom of In, but the molecules NH_3 and $InCl_3$ exist; assuming that 3 atoms of Cl are strictly equivalent to 3 atoms of H, it follows that an atom of N is equivalent to an atom of In. An atom of S cannot be exchanged for an atom of O in the molecule OCl_2; but the molecule SH_2 exists, therefore, on the assumption that H_2 is strictly equivalent to Cl_2; it follows that S is equivalent to O. This conclusion is upheld by the direct exchange of S for O in the molecules SH_2 and OH_2. The conception of equivalency is evidently stretched a little beyond its strict meaning when we say for instance that, because of the existence of the molecules OH_2 and $TiCl_4$, an atom of Ti is equivalent to two atoms of O. But notwithstanding this, the definition of the valency of an atom which has been given may be applied to considerations regarding the structure of molecules. So far as data go, we seem justified in widening the definition of the valency of an atom, and in asserting that this number expresses the maximum number of other atoms, be they monovalent or polyvalent, with which the given atom combines to form a gaseous molecule. Underlying the word *combines* is the conception of *direct* interaction in the molecule. It is not necessary to venture on any hypothesis as to the states of motion of the atoms which form the molecule, or as to the nature of the mutual actions which occur between them; it is only necessary to distinguish direct from indirect action.

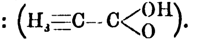
The prevailing notions regarding the structure of molecules are based on that of the valencies of atoms; and this carries with it the conception of each atom being able to act on, and be acted on by, a limited number of other atoms. These conceptions are indicated more or less clearly in the ordinary notation. Thus the so-called structural formulæ (1)



$$H_3{\equiv}C-\underset{\displaystyle OH}{\underset{|}{C}}{\equiv}H_2$$

and (2) $H_3{\equiv}C-O-C{\equiv}H_3$, imply, that each carbon atom in either molecule acts directly on, and is directly acted upon by, 4 other atoms (the C atom is tetravalent), that each oxygen atom acts directly on, and is directly acted on by, 2 other atoms (the O atom is divalent), and that each hydrogen atom acts directly on, and is directly acted on by, a single other atom (the H atom is monovalent). But the distribution of the interatomic reactions is represented as being different in each molecule. In the first, 5 atoms of H are represented as in direct union with (*i.e.* as directly interacting with) atoms of carbon; the sixth atom of H is represented as in indirect union (through an atom of O) with a carbon atom; the atom of O is represented as in direct union with one carbon and one hydrogen atom. In the second molecule, all the H atoms are represented as in direct union with C atoms, and there is also direct action and reaction between the atom of O and each C atom. These formulæ are arrived at after a careful study of the reactions of the compounds; they summarise these properties in the language of a special outcome of the molecular and atomic theory. It would be out of place to pursue the subject of structural formulæ here (*v.* FORMULÆ); these formulæ are supposed to rest on the fundamental conception of the valency of the atom of each element. This conception at once limits the number of atoms with which any specified atom can be directly combined in gaseous molecules; and it enables us to bring together under certain fairly definite expressions (which are, however, very easily misunderstood) regarding the composition of compounds, as composition is viewed by the molecular theory, many facts regarding the functions of compounds gained by the careful study of the behaviour of these compounds under different conditions (*v.* EQUIVALENCY).

We have already somewhat fully discussed the meaning to be given to the term acid; we have learnt that those compounds which contain replaceable hydrogen also contain negative elements. Many gaseous acids are known; the application to these of the conception of structure which springs from that of the equivalency of atoms leads to the view that in the molecule of an acid there is always direct mutual action between those atoms of hydrogen whose function is shortly expressed by the qualifying term *replaceable*, and one or more negative atoms or groups of atoms. Thus, in the molecules HCl, HBr, HI, HF, H(CN), there must be mutual action and reaction between the positive H atom and the negative Cl, Br, I, or F atom, or the negative group of atoms (CN). Again, the reactions of the molecule $C_2H_4O_2$ oblige us to admit that direct mutual action occurs between the atom of replaceable hydrogen and an atom of the negative element oxygen, and that the three atoms of hydrogen which do not act as acidic hydrogen are in direct union with carbon atoms only:



$\left(H_3{\equiv}C{-}C{<}^{OH}_{O}\right)$.

A system of classification of compounds may be developed on the lines of the structure of the molecules of these compounds. If this classification is to be of much permanent value it must be limited to compounds to which the fundamental conceptions of the system can be applied. We have tried to show that this is equivalent to saying that the system must at present be limited to gaseous compounds. But the vast majority of chemical compounds, other than those of carbon, have not been gasified, and most of them appear to be incapable of existing in the gaseous state. Hence a system founded on the conception of molecular structure cannot be strictly applied at present to the bodies which come within the province of inorganic chemistry. Some of the subsidiary conceptions gained as the applications of the system to carbon compounds are developed may, however, be used as aids in classifying non-gasifiable bodies, provided always care be taken not to overstep the limits imposed by the conditions of the inquiry. Thus, arguing from the similarities of properties exhibited by acids as a class, and from what the hypothesis of molecular structure helps us to understand of the connections between the functions of particular atoms and the arrangement of all the atoms in the molecules of gaseous acids, we may conclude that, in the collocations of atoms which (by hypothesis) form the reacting units of non-gasifiable acids, there is more direct mutual action between the atoms of replaceable hydrogen and some negative atoms or groups of atoms, than between those atoms of replaceable hydrogen and the more positive atoms of the reacting atomic complexes. Again, when we have learned from the study of the gaseous compounds of phosphorus that an atom of this element appears to be capable of directly acting on, and being acted on by, not more than five other atoms in a molecule, we may conclude that in the collocations of atoms which (by hypothesis) form the reacting units of the non-gasifiable compounds of phosphorus, each atom of this element is probably in direct union with not more than five other atoms. This tentative conclusion may then be applied to the development of limiting forms for phosphorus compounds; the compositions of these compounds may be represented so that they shall all come under the limiting form RX_5. But it is easy to forget the limits within which such a method as this is of any real help. It is easy to forget that the notion of the equivalency of atoms, on which such a conclusion as that just reached regarding the limiting forms of phosphorus compounds is really based, is a notion which, somewhat vague in itself, becomes vaguer the moment an attempt is made to apply it to discussions about solid and liquid bodies, for which only the outlines of a molecular theory have yet been drawn.

A system of classification, even of gaseous compounds, cannot be reared on the conception of atomic valency pure and simple. If one atom can directly interact with, say, four other atoms, the existence of a vast number of molecules built up by the union of this atom with those of two or three other elements becomes possible. Why do not all these molecules exist? Because, replies the hypothesis of molecular structure, the properties, and hence the possible existence, of a molecule, depend not only on the nature, number, and actual valencies, of the constituent atoms, but also on the manner in which the mutual interatomic reactions are distributed in the molecule. Besides the valencies of the atoms, it is necessary to consider the distributions of the interactions of these atoms. But how can we frame a working hypothesis regarding the distributions of the interatomic reactions which shall help us to understand the structure of the collocations of atoms with which it seems we have to deal in liquid and solid compounds? These interatomic actions may be distributed now in this way, now in that; the effect of this or that reagent may be to cause changes in the distributions of these reactions. We have as yet no solid basis of facts, or even of intelligible hypothesis on which to build. Compounds of about fifty-six elements (excluding carbon) have been gasified; as a rule, not more than six or eight compounds of each element are known in the gaseous state; about sixty of these compounds are available as data on which to base arguments regarding the valencies of perhaps forty-five elementary atoms. Supposing, then, that a system of classification of compounds is to be based strictly on the valencies of the atoms in the molecules of these compounds, the system must be restricted to 200 or 300 compounds, formed by the combinations of about fifty-six elements.

As regards the connections between atomic valencies and atomic weights, it appears that the valencies of the elementary atoms in certain series of elements vary from a minimum value for the first member of the series to a maximum for the middle member, and back again to the minimum value for the last member of the series. Thus take series 2—Li, Be, B, C, N, O, F—the following are the valencies of the atoms of the members of this series so far as these valencies have been established on reasonably satisfactory data (the valency is in each case represented by a Roman numeral placed above the symbol of the element):—

Groups.

	I.	II.	III.	IV.	V.	VI.	VII.
Series 2—	Li^{I}	Be^{II}	B^{III}	C^{IV}	N^{III}	O^{II}	F^{I}

It is possible that the valencies of the elementary atoms vary periodically with variations in the atomic weights of the elements. Should it be established that this is so, we shall have another illustration of the wide application and usefulness of the periodic law. But the classification which is founded on the periodic law rests on this generalisation as a whole, and not on any single property of either elements or compounds. The periodic law insists on the paramount importance of the comparative study of all the properties of elements and compounds; element must be compared with element, compound with compound. Thus, and thus alone, can we hope to gain a final system of chemical classification. Thus, and thus alone, can we expect to trace the fundamental relations which undoubtedly exist between the properties and the composition, and between the changes of properties and changes of composition, of homogeneous kinds of matter. On the basis of the periodic law a scheme of classification of the chemical elements and compounds may be raised, which exhibits (1) the composition of the compounds in so far as this can be shown in the present state of chemical knowledge; (2) the functions of the compounds, that is to say the reactions in which they take part; and (3) the connections between the compositions and the functions of the compounds; and in thus classifying the compounds of the different elements the method at the same time classifies the elements themselves. M. M. P. M.

In connection with the subject-matter of this article the following articles should be read:—Atomic and molecular weights; Chemical change; Equilibrium, chemical; Equivalency; Formulæ; Molecular structure of matter, theories regarding; Periodic law; Physical methods of inquiry used in chemistry. Further details of the properties of the various families of elements and their chief compounds are given in the following articles:—Alkaline earths, metals of the (Ca Sr Ba); Alkalis, metals of the (Li Na K Rb Cs, NH_4—Tl); Boron; Carbon group of elements (C Si—Ti Zr Sn Ce Pb Th); Chromium group (Cr Mo W U); Copper group (Cu Ag, Au); Earths, metals of the (Al Ga In, Sc Y La Yb—Tl); Halogens, the (F Cl Br I, CN—Mn); Hydrogen; Iron group (Fe Ni Co—Mn); Lead; Magnesium group (Be, Mg Zn Cd, Hg); Nitrogen group (N P As V Nb Sb Di Er Bi); Noble metals (Au, Rh Ru Pd, Os Ir Pt); Oxygen group (O S Se Te—Cr Mo W U); Tin group (Sn Ge Pb); Titanium group (Ti Zr Ce Th).

The following memoirs and books may be consulted by those who wish to trace the development of the various schemes of chemical classification which have from time to time prevailed in the science:—

Lavoisier (Compound radicles), *Traité élémentaire de Chimie* (edit. 1789), 1, 197, 209.

Dumas and Boullay (Compound ethers), *A. Ch.* 27, 15 (1828).

Wohler and Liebig (Benzoyl compounds), *A.* 3, 249 (1832).

Berzelius (Radicle of the benzoic compounds), *A.* 3, 282.

Berzelius (Radicles of alcohol and its derivatives), *J.* 1833. 189; *P.* 28, 617.

Liebig (Ethyl), *Handwörterb. d. Chemie* (1te Auflage), article '*Æther*'; *A.* 9, 1.

Liebig (Acetyl, constitution of acetic acid, &c.), *A.* 14, 133.

Dumas (Substitution), *A. Ch.* 56, 143 (1835); *Traité de Chimie appliquée aux Arts*, 5, 99.

Laurent (Nucleus theory), *A. Ch.* 61, 125 (1836).

Gerhardt (Conjugated compounds), *ibid.* 72, 181 (1838).

Dumas (Substitution), *C. R.* 10, 149.

Gerhardt (Atomic weights of oxygen, carbon, &c.), *A. Ch.* [3] 7, 129; 8, 238; *Précis de Chimie organique* (1844), 1, 47).

Gerhardt (Homology), *Précis*, 2, 489.

Laurent (Law of even numbers of atoms; nature of the elements in the free state; monads and dyads), *A. Ch.* [3] 18, 266 (1846); *Chemical Method*, 46–96, *et passim.*

Wurtz (Compound ammonias), *C. R.* 28, 233, 323 (1849); 29, 169; *C. J.* 3, 90.

Hofmann (Compound ammonias), *T.* 1850. 93; *C. J.* 3, 279.

Williamson (Mixed ethers, etherification), *C. J.* 4, 106, 229 (1851).

Williamson (Constitution of salts), *C. J.* 9, 350 (1851).

Gerhardt and Chancel (Constitution of organic compounds), *Compt. chim.* (1851) 7, 65.

Gerhardt (Basicity of acids), *Compt. chim.* (1851) 7, 129.

Gerhardt (Anhydrous organic acids; classification by types), *C. R.* 34, 755, 902 (1852); *C. J.* 5, 127, 226; more fully *A. Ch.* [3] 37, 285; Dumas's Report, *C. R.* 36, 505.

Berthelot (Synthesis of fats; nature of glycerine), *A. Ch.* 61, 216 (1853-54).

Odling (Constitution of salts; polyatomic radicles), *C. J.* 7, 1 (1854).

Wurtz (Theory of glycerine-compounds; polyatomic radicles), *A. Ch.* [3] 43, 493 (1855).

Wurtz (Mixed radicles), *ibid.* 44, 275.

Gerhardt and Chiozza (Amides), *ibid.* 46, 129 (1855–56).

H. L. Buff (Polyatomic radicles), *Pr.* 8, 188 (1856).

Wurtz (Dihydric alcohols), *A.* 100, 110; more fully, *A. Ch.* [3] 55, 400 (1856-59).

Kekulé (Mixed types, radicles, &c.), *A.* 104, 129 (1857).

Kekulé (Ditto; tetravalent character of carbon atom), *ibid.* 106, 129 (1858).

Couper (Valency of carbon and oxygen), *A. Ch.* [3] 53, 504 (1858); *A.* 110, 46 (here followed by critique by Buttlerow, 1859).

Kolbe (Constitution of lactic acid), *A.* 109, 257 (1859); same subject, *ibid.* 113, 223 (1860).

Foster (Nature of radicles and types), *B. A.* 1859, 1.

Wurtz (Basicity of acids), *A. Ch.* [3] 51, 342 (1859).

Cahours (Combining capacity of the elements; limits of combination), *A. Ch.* [3] 58, 5 (1860).

Frankland (same subject), *C. J.* 13, 177 (1860).

Wurtz (Constitution of lactic acid), *A. Ch.* [3] 69, 161 (1860).

Cahours (same subject), *A. Ch.* [3] 62, 257 (1861).

Buttlerow (Valencies of the elements), *Z.* 4, 549 (1861).

Erlenmeyer (same subject), *ibid.* 5, 18 (1862).

Kolbe (Classification of organic bodies), *A.* 113, 293 (1860); Critical Remarks by Wurtz, *Rép. Chim. Pure*, 2, 354.

Lossen (Critical discussion of valency), *A.* 204, 265 (1883).

Lehmann (Physical isomerism), *Z. K.* 1, 97.

Mendelejeff (Periodic law), *C. N.* 40 and 41. Papers on the applications of the periodic law are numerous; *v.* especially Carnelley, *P. M.* [5] 8, 315; 18, 1; 20, 259, &c.

Laurent, *Méthode de Chimie*, 1854; Cavendish Society's translation, 1855.

Gerhardt, *Traité de Chimie organique*, 4 vols. 1853-56; especially 1, 121–142; 4, 561 808.

Kekulé, *Lehrbuch der organischen Chemie*, vol. 1 (1859-61).

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CLOVES, OIL OF. Contains eugenol $C_{10}H_{12}O_2$, and a terpene $C_{15}H_{24}$ (254° cor.); V.D. 7·7 (Ettling, *A.* 9, 68; Bruning, *A.* 104, 205; Williams, *A.* 107, 242; Church, *C. J.* 28, 113). The terpene is converted by Br into $C_{15}H_{22}$ (250°–260°)(Beckett a. Wright, *C. J.* 29, 1).

CNICIN $C_{42}H_{56}O_{15}$ (?). Occurs in the leaves of *Centaurea benedicta* or *Cnicus benedictus* and bitter plants of the order *Compositæ* sub-order *Cynarocephalæ* (Morin, *J. Chim. Méd.* 3, 105; Scribe, *C. R.* 15, 803). Silky needles, with bitter taste; v. sol. alcohol, v. sl. sol. ether; sl. sol. hot water. Dextro-rotatory, $[\alpha] = 131°$ (Bouchardat). Its solution is rendered turbid by long boiling. H_2SO_4 forms a blood-red solution. Conc. HClAq becomes green, and deposits a resin on warming.

COAL TAR. The oily product of the distillation of coal contains benzene, toluene, *o*-, *m*-, and *p*-, xylene, naphthalene, anthracene, phenol, *o*-, *m*-, and *p*-, cresol, and ammonia. The minor constituents are water, hydrogen, nitrogen, carbonic oxide, COS, cyanogen, CS_2, H_2S, HCN, CO_2, methane, ethylene, acetylene, propylene, allylene, butylene, crotonylene, amylene, hexylene, **hexinene, ennane, decane, styrene, mesitylene, ψ-cumene, terpenes, naphthalene dihydride, methyl-naphthalene, di-methyl-naphthalene, diphenyl, acenaphthene, fluorene, phenanthrene, fluoranthene, ψ-phenanthrene, methyl-anthracene, pyrene, chrysene, picene, acetic acid, acetonitrile, thiophene, methyl-thiophene, di-methyl-thiophene, phenyl thiocarbimide, pyrocreosols, carbazole, phenyl-naphthyl-carbazole (phenylene-naphthylene-imide), xylenol, benzoic acid, (α)- and (β)-naphthol, pyridine, pyrrole, methyl-pyridine, di-methyl-pyridine, tri-methyl-pyridine, aniline, quinoline, methyl-quinoline, parvoline, coridine, rubidine, viridine, lepidine, cryptidine, and acridine** (*cf.* Schultz, *Die Chemie des Steinkohlentheers*). Many of the hydrocarbons present in coal tar are probably formed from phenols by splitting off water, and reduction (Schulze, *A.* 227, 152). Others are formed by the action of heat on simpler hydrocarbons. Thus marsh gas is converted by passage through a red-hot tube into benzene, propylene, and naphthalene; ethane gives C_2H_4 and hydrogen; ethylene gives ethane and acetylene; acetylene gives hydrogen, ethane, ethylene, benzene, styrene, and naphthalene; benzene gives diphenyl and hydrogen; while a mixture of benzene and ethylene gives anthracene (Berthelot, *A.* 142, 254; Schultz, *A.* 174, 203; 203, 118). Most of the bases are probably formed either by the action of ammonia on the phenols, or by the condensation of bases so formed with themselves, with other bases, with phenols, or with unsaturated hydrocarbons.

COBALT Co. At. w. 58·8. Mol. w. unknown as element has not been gasified. [c. 1500°] (Pictet, *C. R.* 88, 1317). S.G. 8 5 8·7 (*v.* Playfair a. Joule, *C. S. Mem.* 3, 57). S.G. 8·96 (Rammelsberg, *P.* 78, 93). S.H. ·107 (Regnault, *A. Ch.* [3] 63, 5). $V_t = V_0 (1 + 3 \times \cdot 0000123 6 t)$. $t = 40°$ (Fizeau, *C. R.* 68, 1125). E.C. at 0° (Hg at 0° = 1) 9·685 (Matthiesen a. Vogt, *P. M.* [4] 26, 242). T.C. (Ag = 100) 17·2 (Barrett, *J.* 1873. 131). S.V.S. c. 6·84. H.C. $[Co^2,O^4,3H^2O] = 149,380$ (*Th.* 3, 306).

Occurrence.—The metal is found in small quantities (1 p.c.) in some meteorites. Chiefly as *smaltine*, $CoAs_2$ in which Co is more or less replaced by Ni and Fe; and *cobalt-glance*, CoAsS with Co partially replaced by Fe and Ni, Co compounds also occur as oxide, sulphate, arsenate, &c., chiefly with compounds of Ni, Fe, and Mn. Compounds of Co were used for producing blue glasses in ancient times. 'Smalt' was prepared in Saxony in the 16th century. Cobalt was first recognised as an element by Brandt in 1735. The name is said to be derived from 'Kobold' (= sprite or goblin) a term applied by miners in the middle ages to minerals which were employed in the arts, but from which no useful metal could be extracted.

Formation.—The ore is roasted to partly remove arsenic and sulphur; the residue is dissolved in HClAq with a little HNO_3; Fe is ppd. by CaO_2H_2; Cu, Bi, &c. are ppd. by H_2S; addition of bleaching powder then pps. $Co_2O_3.xH_2O$; this is heated, and the Co_3O_4 formed is reduced by heating with charcoal.

Preparation.—1. The chief impurities to be removed are As and other metals ppd. by H_2S, Fe, and Ni. The roasted ore freed from gangue may be fused with nitre, treated with water to dissolve K arsenate, the residue dissolved in *aqua regia*, evaporated, diluted, saturated with H_2S, and filtered; the filtrate may then be mixed with so much of a ferric salt that a brown pp. (ferric arsenite and $Fe_2O_6H_6$) forms on partial neutralisation, K_2CO_3Aq is then added so long as the pp. is brown, and until a few drops of the filtrate give a reddish pp. (showing ppn. of Ni) with alkali; almost every trace of As is thus removed; the filtrate may be acidulated with HCl and reppd. by H_2S. To the filtrate (which should be only slightly acid) solution of bleaching powder or NaClO is added, so long as the pp. is black (Co_3O_4), a reddish-brown colour indicates ppn. of Ni oxides; the pp. is washed, and dissolved in nitric acid, the liquid is concentrated and neutralised by KOH, mixed with KNO_2Aq, strongly acidified by acetic acid, and allowed to stand for a few days; the pp. of K-Co nitrite is washed, dried, and strongly heated; K is removed by washing with water; the residual Co oxide is dissolved in oxalic acid, and the Co oxalate is reduced by strongly heating in a closed crucible (Hermbstadt, *J. pr.* 31, 105; Patera, *J. pr.* 67, 14).—2. The oxide, prepared as described in 1, is reduced in a stream of H at temp. above 320° (Muller, *P.* 136, 51).—3. The oxide is dissolved in HClAq and the solution is evaporated to crystallisation, the crystals of $CoCl_2.6H_2O$ are dried and heated in a stream of Cl; and the $CoCl_2$ thus obtained is reduced by heating in H (Peligot, *C. R.* 19, 670).—4. A solution of the oxide is saturated with NH_4 oxalate, and the liquid is warmed, a little solid NH_4 oxalate is dissolved in the hot liquid which is then electrolysed, using a Pt basin as negative, and a piece of Pt foil as positive, electrode (Classen a. Von Reis, *B.* 14, 1622).

Properties.—Steel-grey, lustrous, crystalline plates; nearly white when polished; hard; somewhat malleable; very ductile at red heat and upwards; slightly magnetic, even at full red heat (Pouillet). The compact metal does not oxidise in air at ordinary temperatures, but when heated it forms Co_3O_4; the finely divided metal obtained by reducing the oxide or chloride in H at moderate temperatures is pyrophoric. Combines directly with Cl. Oxidised superficially by H_2O_2Aq. Decomposes steam at red heat, and NH_3 to N and H. Dissolves in mineral acids forming cobaltous salts. Cobalt wire heated till superficially oxidised, and at once plunged into fuming nitric acid, does not dissolve; it shows 'passivity' (Nicklès, *C. R.* 38, 284) due either to the formation of a protecting layer of N oxides, or to a layer of cobalt oxide (*cf. passivity of iron*, under Iron). Co in thin leaves is said to absorb H much as Pd does (Bottcher, *J.* 1874. 295).

Cobalt is distinctly metallic in its chemical behaviour; CoO forms a series of well-marked normal salts, many basic salts are also known; Co_2O_3 dissolves in acids probably forming salts, but these are very soon decomposed to cobaltous salts; double cobaltic salts are, however, stable, *e.g.* $Co(NO_2)_3.3KNO_2$ (*v.* also Cobaltamines). When CoO is added to molten KOH, the compound $(Co_3O_5)_4.K_2O$ is said to be produced, in which Co forms part of the acid radicle (*v.* Cobaltates). The sulphides of Co show no acidic character.

The atomic weight of Co has been determined (1) from analyses of the sulphate and chloride (Marignac, *Ar. Sc.* 1, 373); (2) by reduction of CoO in H (Russell, *C. J.* [2] 1, 51); (3) by reduction of NH_4-Co cyanide and phenylammonium cobalt cyanide (Weselsky, *B.* 2, 592); (4) by reduction (by heat) of strychnine- and brucine-cobalt cyanide (Lee, *C. N.* 24, 234); (5) by reducing CoO in H (Zimmermann, *A.* 232, 324). Determinations of the S.H. have shown that 58.8 and not a multiple of this number is to be adopted. This result has been confirmed by the isomorphism of several Co salts with the corresponding salts of Ni and Fe.

Cobalt is very closely related in its chemical properties to Ni, it is classed with this metal and Fe, and it also shows analogies with Mn; *v.* Iron group of elements.

Reactions and *Combinations.* 1. With *steam* at red heat forms CoO and H.—2. Strongly heated in *air* burns to Co_3O_4. 3. Decomposes *ammonia* at red heat to N and H.—4. Dissolves in *mineral acids* with formation of salts; with H_2SO_4 evolves SO_2, and with HNO_3 gives N oxides. Thomsen (*Th.* 3, 306) gives these thermal data; $[Co,H^2SO^4Aq] = 19,710$ giving $CoSO_4 + H_2$; $[Co,H^2Cl^2Aq] = 16,190$.—5. Combines with *chlorine, bromine, and iodine*, by heating in contact with these elements, forming $CoCl_2$, $CoBr_2$, and CoI_2, respectively. $[Co,Cl^2] = 76,480$; $[Co,Cl^2,Aq] = 94,820$; $[Co,Br^2,Aq] = 72,910$; $[Co,I^2,Aq] = 42,520$ (*Th.* 3, 306).—6. Heated with *sulphur* forms CoS and Co_4S_3.—7. Combines with *selenion* to form CoSe, by heating the two elements together (*v.* Cobalt, selenide of).—8. Combines with *arsenic* (*v.* Cobalt, arsenides of).—9 Absorbs (? combines with) small quantities of *carbon* when strongly heated with it, forming a hard grey mass resembling steel.—10. Forms *alloys* with several metals, especially Sb, Bi, Au, Fe, Pb, Pt, Ag, Sn, and Zn; little is known of these bodies.

Detection and estimation.—Co compounds give a clear blue colour with a bead of *borax* or *microcosmic salt* in both blowpipe flames. Black CoS is ppd. by *alkaline sulphides*, but not by H_2S in acid solutions. *Ammonia* pps. blue basic salts, soluble in excess to a reddish liquid which absorbs O from the air and becomes brownish; KOHAq pps. part of the Co as hydrated oxide from this solution. Traces of Co are detected by adding excess of NH_3Aq, and then K_3FeCy_6Aq, when a dark yellowish red colour is produced (Skey, *C. N.* 15, 111); or by adding excess of KCNAq followed by NH_4 sulphide, when a blood-red colour is formed which slowly disappears (Tattersall, *C. N.* 39, 66; Papasogli, *B.* 12, 297). Co may be estimated by ppn. as oxalate, which is then decomposed by heat to metal. The Co may be separated from Ni by evaporating an acid solution to a small bulk, adding slight excess of KOHAq, acidifying with acetic acid, adding excess of a conc. solution of KNO_2 strongly acidified by acetic acid, allowing to stand for 24 hours in a warm place, and washing the ppd. $Co_2(NO_2)_6.6KNO_2$ with solution of 1 part K acetate in 9 parts H_2O. The pp. is dissolved in HClAq; liquid is evaporated until very conc. and all free acid is removed, $K_2C_2O_4Aq$ is added drop by drop until the pp. which forms is dissolved, a *little* water is added, the liquid is heated to boiling, and rather more than an equal volume of 80 p.c. acetic acid is added *very slowly*; after standing 6 hours at about 50° the ppd. Co oxalate is filtered off, washed with a mixture of equal volumes of conc. acetic acid, alcohol, and water, and dried; it is heated in a closed crucible, then strongly in the air (to oxidise C), and the oxide is reduced by strongly heating in H. After weighing, the Co should be washed in hot water and again heated in H (Classen, *Fr.* 18, 189). Classen recommends the electrolytic estimation of Co by depositing the metal from a solution in excess of warm $K_2C_2O_4Aq$ (*v.* Classen's *Quantitative Analyse durch Electrolyse*, Berlin, 1886. A description of the apparatus will be found in Dittmar's *Exercises in Quantitative Chemical Analysis*, Glasgow, 1887). Wolff (*Fr.* 18, 38) proposes to determine minute quantities of Co by a spectroscopic method based on the absorption-spectrum of very dilute solutions of Co to which excess of NH_3Aq and a little NH_4SCy have been added.

Technical applications.—By adding a fraction of a per cent. of Mg to Co an easily worked metal is obtained, which is very compact and lustrous, and resists the action of the air (Fleitmann, *B.* 12, 454; *Biedermann's Chem.-techn. Jahrber.* 1884-5. 25). Many metals may be covered with a thin deposit of Co by electrolysing a fairly conc. solution of $CoCl_2.NH_4Cl$ (Bottcher, *W. J.* 1876. 219; Gaiffe, *C. R.* 87, 100) (*v.* COBALT COLOURING MATTERS, p. 229.)

References.—Besides those in the text the following are of importance: (1) Regarding the metallurgy and preparation of Co; Manhès (*B.* 17, 622), Wöhler (*P.* 6, 227), Liebig (*P.* 18, 164), Langier (*A. Ch.* 9, 267), Stromeyer (*A.* 96, 218). (2) Regarding the properties of Co; Deville (*D. P. J.* 140, 428), Barrett (*J.* 1873. 131). (3) Regarding technical applications of Co; Wiggin (*W. J.* 1881. 69; *v.* also *W. J.* 1883. 149). (4) Regarding separation and estimation of Co; Fischer (*P.* 74, 115), Braun (*Fr.* 7, 313), Liebig (*A.* 65, 244; 87, 128), Fleischer (*J. pr.* 1870, 2, 48), Donath (*B.* 12, 1868).

Cobalt, alloys of. Little is known of these bodies; Co seems to form alloys with Sb, Bi, Au, Fe, Pb, Pt, Ag, Sn, and Zn.

Cobalt, ammonia compounds of *v.* COBALTAMINES, p. 222.

Cobalt, antimonate of. $Co(SbO_3)_2.xH_2O$ (Heffter, *P.* 86, 418; *cf.* vol. i. p. 285).

Cobalt, arsenates of. $CoH_4(AsO_4)_2$ and $Co_3(AsO_4)_2.8H_2O$; *v.* vol. i. p. 308.

Cobalt, arsenides of. Co and As are said to form a grey-black, porous, mass, when heated together in the ratio of 2 parts Co to 3 parts As. The mineral *smaltine* is more or less pure Co arsenide, $CoAs_2$: and *skutterudite* is nearly pure $CoAs_3$.

Cobalt, arsenite of. $Co_3H_6(AsO_3)_4.H_2O$; *v.* vol. i. p. 306.

Cobalt, borate of. Probably $2CoB_2O_4.CoO_2H_2.3H_2O$ (H. Rose, *P.* 88, 299).

Cobalt, bromide of. $CoBr_2$. Mol. w. unknown. $[Co,Br^2,Aq] = 72,940$ (*Th.* 3, 306). A green, deliquescent, lustrous solid; prepared either by heating Co in Br vapour (Rammelsberg, *P.* 55, 244); or by warming Co in contact with Br and H_2O, evaporating over H_2SO_4, drying the crystals of $CoBr_2.6H_2O$, and heating to c. 130° (Hartley, *C. J.* [2] 12, 214). The crystals of $CoBr_2.6H_2O$ melt at 100°, giving the purple-grey hydrate $CoBr_2.2H_2O$ (Hartley). $CoBr_2$ absorbs NH_3, forming $CoBr_2.6NH_3$, from which all NH_3 can be removed by heat (*v.* COBALTAMINES). $CoBr_2Aq$ and $PtBr_4Aq$ evaporated yield carmine, rhombohedral, very deliquescent, crystals of $CoBr_2.PtBr_4.12H_2O$; S.G. 2·763 (Topsoë, *J.* 1868. 275).

Cobalt bromide, hydrated; *v.* COBALT, BROMIDE OF.

Cobalt, carbides of. Co absorbs C when heated with charcoal, forming a hard, grey, steel-like solid. It is not known whether definite carbides are formed or not.

Cobalt, chloride of, $CoCl_2$. Mol. w. unknown. $[Co,Cl^2] = 76,480$; $[CoCl^2,Aq] = 18,340$ (*Th.* 3, 306). Absorption-spectrum, *v.* Russell, *Pr.* 32, 258.

Preparation.—1. CoO, or $CoCO_3$, is dissolved in dilute HClAq, the solution is evaporated until a blue-green solid separates, which is sublimed in a stream of dry Cl or dry HCl.—2. Finely divided Co or CoS is heated in a stream of Cl.—3. $CoCl_2.6H_2O$, obtained by crystallising solution of CoO in HClAq, is heated to 120°; traces of oxychloride are always formed thus (Potilitzin, *B.* 17, 276).

Properties and Reactions.—Blue crystalline scales: easily soluble in water forming reddish liquid, also in absolute alcohol. $CoCl_2Aq$ of different S.G. contains as follows (Franz, *J. pr.* [2] 5, 271):—

S.G.	$CoCl_2$ p.c.	S.G.	$CoCl_2$ p.c.
1·0496	5	1·2245	20
1·0997	10	1·3002	25
1·1579	15	1·3613	saturated at 17·5°.

A saturated alcoholic solution contains 23·6 p.c $CoCl_2$, appears blue by reflected light and almost black by transmitted light, becomes colourless when diluted so that one part $CoCl_2$ is contained in 10,000 parts of solution, but blue colour returns on warming; S.G. of this solution is 1·0107. Addition of water to the blue alcoholic solution produces violet and then red colour; a method of determining water in alcohol or in organic compounds miscible with alcohol has been founded on this reaction (Winkler, *J. pr.* 91, 209). An aqueous solution of $CoCl_2$ becomes blue on addition of conc. HClAq, H_2SO_4, or other dehydrating agent; also on heating, the temperature of change being the lower the more conc. is the solution, thus a 50 p.c. solution changes colour at 60°–100°, a 25 p.c. solution at 85°–135°, and a 10 p.c. solution at 180°–207° (Tichborne, *J.* 1872. 27). Addition of HCl to conc. $CoCl_2Aq$ pps. crystals containing from 1 to $1\frac{1}{2}$ H_2O (Ditte, *A. Ch.* [5] 22, 551). The change of colour of solution of $CoCl_2$ from blue to red is accompanied by hydration (Potilitzin, *B.* 17, 276); it is not an isomeric change as supposed by Bersch (*W. A. B.* 56, 724).

Combinations.—1. With *water* to form various hydrates (*v.* Potilitzin, *B.* 17, 276). The hexahydrate, $CoCl_2.6H_2O$, separates by carefully evaporating a red solution of CoO or $CoCO_3$ in HClAq; dark red monoclinic crystals; S.G. = 1·84; lose water at 30°–35°, and at 45°–50° form the dihydrate; slowly lose water over H_2SO_4 forming the dihydrate; $[CoCl^2,6H^2O] = 21,190$;

$[CoCl^2.6H^2O,Aq] = -2850$ (*Th.* 3, 306). The dihydrate, $CoCl_2.2H_2O$, forms a rose-red finely crystalline powder; prepared as described above; absorbs water from the air forming the hexahydrate. The monohydrate, $CoCl_2.H_2O$, is obtained by heating the dihydrate to c. 100°, or by slowly evaporating a solution in absolute alcohol of the hexa- or di-hydrate, the temperature being gradually raised to 95°. Lustrous, violet-blue, crystalline needles: dehydrated at 110°–120°. — 2. With *ammonia* to form the compounds $M.6NH_3$, $M.4NH_3$, and $M.2NH_3$ where $M = CoCl_2$ (*v.* COBALTAMINES). — 3. With *ammonium chloride* to form $CoCl_2.NH_4Cl.6H_2O$; prepared by evaporating a mixture of solution of CoO in 2 parts HClAq and NH_3 in 1 part HClAq (Hantz, *A.* 66, 284); not obtained from mixed solutions of $CoCl_2$ and NH_4Cl (Merrick, *J.* 1876. 251); forms ruby-red, deliquescent crystals. — 4. With *aniline, paratoluidine*, and *xylidine.* The aniline compounds are $CoCl_2.(C_6H_5.NH_2)_2$ and $CoCl_2(C_6H_5.NH_2)_2.2C_2H_6O$; the former, lustrous blue crystals, is obtained by dissolving $CoCl_2$ in hot aniline and crystallising from absolute alcohol; the latter, rose-red leaflets, by adding aniline to an alcoholic solution of $CoCl_2$; at 100° alcohol is completely removed. The toluidine and xylidine compounds, obtained similarly to the aniline compound, are blue needles: $CoCl_2.(C_6H_4.CH_3.NH_2)_2$ and $CoCl_2.(C_6H_3(CH_3)_2.NH_2)_2$ (Lippmann a. Vortmann, *B.* 11, 1069; 12, 79).—5. With *cadmium chloride, gold chloride*, and *zinc chloride* to form $CoCl_2.2CdCl_2.12H_2O$, $CoCl_2.2AuCl_3.8H_2O$, and $CoCl_2.ZnCl_2.6H_2O$, respectively; by evaporating mixed solutions of the constituent chlorides. 6. With *cobaltous oxide*; when dilute NH_3Aq is added drop by drop to boiling $CoCl_2Aq$ a blue pp. is formed, which turns peach-red; this pp. when dried probably has the composition $2CoCl_2.6CoO.7H_2O$ (Habermann, *M.* 5, 442).

Cobalt chloride, hydrated; *v.* COBALT, CHLORIDE OF; *Combinations*, No. 1.

Cobalt, chromates of; *v.* CHROMATES.

Cobalt, cyanides of, also Cobalto- and Cobalticyanides; *v.* CYANIDES.

Cobalt, fluoride of, $CoF_2.2H_2O$. Mol. w. unknown. Rose-red crystals; by dissolving CoO in excess of HFAq; soluble in Aq containing HF, or in a little cold water; decomposed by much hot water to oxyfluoride $Co_2OF_2.H_2O$ (Berzelius). Combines with *potassium fluoride, sodium fluoride*, and *ammonium fluoride*, to form double salts; $CoF_2.KF.H_2O$, $CoF_2.NaF.H_2O$, and $CoF_2.2NH_4F.2H_2O$ (Berzelius; Wagner, *B.* 19, 897).

Cobalt, haloid compounds of.—These compounds all belong to the form CoX_2; X = F, Cl, Br, or I. None has been gasified, and therefore the molecular weight of none is known with certainty. These compounds are greenish-blue solids; all form hydrates, which are reddish. All are soluble in water, and all seem to form double compounds with alkali haloid compounds. A very few oxyhaloid compounds have been prepared.

Cobalt, hydrated oxides of; *v.* COBALT, OXIDES AND HYDROXIDES OF.

Cobalt, hydroxides of; *v.* COBALT, OXIDES AND HYDROXIDES OF.

Cobalt, iodide of, CoI_2. **Mol. w. unknown.** A black, graphite-like, solid; obtained by digesting Co with water and iodine, filtering, evaporating the red liquid till it gets thickish, cooling over H_2SO_4, and heating the crystals to 130° (Hartley, *C. J.* [2] 12, 502). The liquid prepared as described yields green crystals of $CoI_2.2H_2O$; these are exceedingly deliquescent. When the same solution is kept at 16° or so for some days red crystals of $CoI_2.6H_2O$ separate (Hartley; Erdmann, *J. pr.* 7, 354; Rammelsberg, *P.* 48, 155). CoI_2 combines with NH_3 to form $CoI_2.4NH_3$ (Rammelsberg, *P.* 55, 245).

Cobalt, oxides and hydroxides of.—Cobalt forms three well-marked oxides: CoO, Co_3O_4, and Co_2O_3; four other oxides are known, which are usually regarded as compounds of the first and third of these, viz. $Co_2O_3.2CoO$, $Co_2O_3.3CoO$, $Co_2O_3.4CoO$, and $Co_2O_3.6CoO$. The monoxide CoO is distinctly basic; the sesquioxide Co_2O_3 dissolves in acids, probably with formation of salts, but very few salts corresponding to this oxide have been obtained as they are very easily reduced to salts of CoO; the other oxides do not form corresponding salts. The monoxide is stable when heated to a moderate temperature, but at full redness it is oxidised to Co_3O_4; Co_2O_3 is deoxidised by heating strongly with formation of Co_3O_4. Several hydrates of the various oxides are known.

I. COBALTOUS OXIDE CoO. (*Cobalt monoxide, cobalt oxide.*) Mol. w. unknown. A greenish-brown powder, slightly hygroscopic. S.G. 5·59 to 5·75 (Playfair a. Joule, *C. S. Mem.* 3, 57). Prepared by heating $CoCO_3$ or $Co(OH)_2$ (*q. v.*) in complete absence of air (Beetz, *P.* 61, 473); or by heating $CoCl_2$ in steam (Schwarzenberg, *A.* 97, 211); or by heating Co_3O_4 in a stream of CO_2 (Russell, *C. J.* 16, 51). CoO is unchanged in air, but when strongly heated it is oxidised to Co_3O_4; it is reduced to Co by heating in H or CO, or with C; it is quickly changed to CoS by heating in H_2S.

COBALTOUS HYDROXIDE $Co(OH)_2$. (*Cobalt hydrate. Hydrated cobaltous oxide.*) $[Co,O,H^2O] = 63,400$ (*Th.* 3, 306). Obtained by adding potash to solution of a cobaltous salt in absence of air; the pp. is a blue basic salt, which slowly changes to the rose-red hydrate; the change is quickened by heating (Winkelblech, *A.* 13, 148, 253; Beetz, *P.* 61, 473). If potash is added to a boiling solution the pp. contains alkali and some basic salt (Fremy, *A.* 80, 277; 83, 227, 289). A rose-red powder; absorbs O from air turning brown; heated in absence of air gives CoO. Cobaltous oxide and hydroxide dissolve in acids forming stable cobaltous salts (*v.* COBALT, SALTS OF, p. 221). $[CoO^2H^2,H^2SO^4Aq] = 24,670$; $[CoO^2H^2,H^2Cl^2Aq] = 21,140$ (*Th.* 3, 307).

II. COBALTIC OXIDE Co_2O_3. (*Cobalt sesquioxide. Cobalt peroxide.*) Mol. w. unknown. A steel-grey, lustrous solid. Heated in air gives Co_3O_4. Dissolves in conc. acids, but very few salts have been obtained corresponding to the oxide; solution in conc. cold acetic acid gives brown pp. of $Co_2O_3.3H_2O$ with an alkali; some double salts are known, *e.g.* $Co_2(NO_2)_6.6KNO_2$ (*v.* COBALT, SALTS OF, p. 221). Prepared by gently-heated $Co2NO_3$ so long as reddish vapours are evolved, powdering finely and again gently heating; or by heating $Co_2O_3.3H_2O$ to 600°–700°.

Cobaltic hydroxides. The compound $Co_2(OH)_6$ or $Co_2O_3.3H_2O$ is obtained by exposing a solution of a cobaltous salt, with excess of NH_3Aq added, to the air until brown, and ppg. by KOHAq; or by ppg. a cobaltous salt solution by a hypochlorite in presence of alkali; or by passing Cl into, or adding BrAq to, $Co(OH)_2$ or $CoCO_3$ suspended in water; the pp. is dried by pressing between paper. A dark-brown powder $[Co^2,O^3,3H^2O] = 149,380$; $[2CoO^2H^2,O,H^2O] = 22,580$ (*Th.* 3, 306). By drying at 100°, or by prolonged exposure over H_2SO_4, the hydrate $Co_2O_3.2H_2O$ [? $Co_2O(OH)_4$] is obtained. The same hydrate is formed as a black lustrous deposit on the positive pole, when a slightly alkaline solution of cobaltous-potassium tartrate is electrolysed, using Pt electrodes (Wernicke, *P.* 141, 119); S.G. as thus obtained = 2·483. The hydrate $3Co_2O_3.2H_2O$ is obtained by heating $CoCl_2$ and $Co_2(NH_3)_{10}Cl_6$ in the ratio 2:1 mols., with water in a open vessel (Mills, *P.M.* [4] 35, 257).

The cobaltic hydrates lose water when gently heated, giving Co_2O_3; when strongly heated they yield Co_3O_4. They dissolve in *cold* conc. acids, forming brown solutions; these solutions are decomposed on warming and thus give cobaltous salts; the solution in conc. acetic acid is fairly stable; potash pps. $Co_2O_3.3H_2O$ from this solution. Freshly ppd. $Co_2O_3.3H_2O$ dissolves in neutral $(NH_4)_2SO_4$Aq forming a solution of $Co_2O_3.10NH_3.6SO_2$ (Geuther, *A.* 128, 157).

III. Cobalto-cobaltic oxide Co_3O_4. (*Black oxide of Cobalt.*) Mol. w. unknown. Obtained by strongly heating in air, or in O, CoO, $Co(OH)_2$, Co_2O_3 or any of its hydrates, $CoCO_3$, $Co(NO_3)_2$, or CoC_2O_4. A black amorphous powder which slowly absorbs water from the air. S.G. 5·833–6·296 (Rammelsberg, *J.* 2, 282). Obtained as lustrous, metal-like, greyish-black microscopic octahedra, by strongly heating a mixture of $CoCl_2$ and NH_4Cl in a stream of air or O, or a mixture of CoC_2O_4 and NH_4Cl in O, and treating the residue with hot conc. HClAq. The crystals are unacted on by many conc. acids, but dissolve slowly in conc. H_2SO_4 (Schwarzenberg, *A.* 97, 211); they are non-magnetic.

Hydrates of cobalto-cobaltic oxide. Three have been described. $Co_3O_4.2H_2O$, obtained by exposing to ordinary air Co_3O_4 prepared by heating $CoCO_3$; $Co_3O_4.3H_2O$, obtained by boiling a solution of roseo-cobaltic sulphate (Genth a. Gibbs, *Am. S.* 23, 257); $Co_3O_4.7H_2O$, obtained by allowing $Co(OH)_2$ ppd. by adding excess of alkali to a cobaltous solution to stand in the air (Fremy).

IV. Other cobalto-cobaltic oxides. (i.) $Co_2O_3.2CoO$; a black powder, obtained by heating dried $CoCO_3$ to 100°–150° in a closed crucible, or by heating luteo- or purpureo-cobalt chloride with 30–40 parts water to 70°–100° in a sealed tube (Mills, *P. M.* [4] 35, 257). (ii.) $Co_2O_3.3CoO$; obtained by heating purpureo-cobalt chloride with 2 mols. $CoCl_2$ and some water to 100° in a sealed tube (Mills, *l.c.*). (iii.) $Co_2O_3.4CoO$; a black powder, unchanged by boiling with HNO_3 or H_2SO_4, obtained by strongly heating cobaltous salts in air. (iv.) $Co_2O_3.6CoO$; obtained with $6H_2O$ by adding NH_3Aq to $Co(NO_3)_2$Aq and allowing to stand in air till pp. is yellow.

Cobalt, oxyhaloid compounds of. Very few of these compounds have been prepared. $2CoCl_2.6CoO.7H_2O$, *v.* Cobalt, chloride of; *Combinations*, No. 6. $CoF_2.CoO.H_2O$, *v.* Cobalt, fluoride of.

Cobalt, oxysulphide of, Co_2OS. ($=CoO.CoS$). Dark-grey powder; by heating $CoSO_4$ in H. Dilute acids dissolve CoO; conc. acids also evolve H_2S; heated, gives CoO and SO_2.

Cobalt, phosphide of, Co_3P_2. Black powder; obtained by ppg. $CoCl_2$Aq by Na_2HPO_4Aq and heating the ppd. phosphate in a stream of H; also by heating $CoCl_2$ in PH_3. Insoluble in conc. HClAq; easily soluble in HNO_3Aq. Co and P combine, by heating Co with a mixture of P_2O_5 and charcoal.

Cobalt, salts of. *Compounds obtained by replacing the H of acids by Co.* Many of these salts are known; most of them belong to the class of *cobaltous salts* CoX_2 where $X = Cl, NO_3, \frac{SO_4}{2}, \frac{2}{3}PO_4$, &c.; a few double *cobaltic salts* CoX_3 are known. The Co salts are generally obtained by dissolving CoO or $CoO.H_2O$ in acids, or by double decomposition from other Co salts. Cobaltous haloid salts, sulphate, nitrate, and some others, are soluble in water; the carbonate and phosphate, &c., are insoluble. Co forms many basic salts. Aqueous solutions of cobaltous salts are generally pink; when very conc. they usually become blue to blue-green; this colour-change is accompanied by dehydration and rehydration (*cf.* Cobalt, chloride of; *Properties and Reactions*). For some account of the resemblances between Fe, Ni, and Co *v.* Iron Group of Metals. Cobaltous salts closely resemble Ni salts; many of them are also very similar to, and isomorphous with, ferrous salts. Cobaltic hydrate $Co_2O_3.3H_2O$ dissolves in conc. cold acids probably forming cobaltic salts; on warming, these solutions are generally quickly decomposed with production of cobaltous salts; a solution in acetic acid is fairly stable. When KNO_2 is added to an acetic acid solution of a cobaltous salt a pp. of the double cobaltic salt $Co(NO_2)_3.3KNO_2$ is obtained. As no compound of Co has been gasified the formulæ of the Co salts are not necessarily molecular. The chief salts of oxyacids are the *carbonates*, *nitrates*, *phosphates*, and *sulphates*; *chlorate*, *bromate*, *iodate*, *nitrite*, *phosphite*, *sulphite*, and a few others, are also known (*v.* Carbonates, nitrates, &c.). A great many double compounds of Co salts with ammonia are known (*v.* Cobaltamines, p. 222).

Cobalt, selenide of. CoSe. Co and Se combine when heated together, forming a metal-like, lustrous, greyish mass, which is fusible at red heat (Berzelius). The compound CoSe is obtained by passing vapour of Se over hot Co in an atmosphere of H; S.G. 7·65; when melted under borax it forms a yellow, crystalline, metal-like solid (Little, *A.* 112, 211).

Cobalt, sulphides of. Co and S combine directly in different proportions. Sulphides are also formed by adding alkali sulphides to cobaltous salts, and by passing H_2S into an acetic acid solution of Co_2O_3, or CoO, and in various other ways. The following sulphides are known: Co_4S_3, CoS, Co_3S_4, Co_2S_3, CoS_2; these are the simplest formulæ that can be given, but they are not necessarily molecular. The sulphides of Co are basic; CoS combines with As_2S_3 and Sb_2S_3.

I. Cobaltous sulphide CoS. (*Cobalt monosulphide.*) Occurs native as *Syepoorite.* Prepared by heating Co with S, or CoO with S, or $CoSO_4$ with BaS and excess of NaCl; forms bronze-coloured, lustrous needles, soluble in acids. Also obtained as a black amorphous powder by adding NH_4 sulphide to an aqueous solution of a cobaltous salt, or by passing H_2S into a dilute acetic acid solution of CoO, or into water holding $Co(OH)_2$ in suspension; the black pp. is soluble in dilute mineral acids, but not in acetic acid; insoluble in alkali sulphides; when moist it oxidises rapidly in air to $CoSO_4$. Non-magnetic (Hjordtdahl, *C. R.* 65, 75). Compounds of CoS with As and Sb sulphides, $M_2S_3.2CoS$, are obtained by adding Co solutions to Na thio-arsenite, &c.

II. Cobaltic sulphide Co_2S_3. (*Cobalt sesquisulphide.*) Occurs native as *Cobalt-pyrites* in octahedra. Prepared by heating CoS or $Co(OH)_2$ in a stream of H_2S, or by strongly heating a mixture of CoO, S, and KOH, and washing with water; forms a graphite-like crystalline powder. Also obtained as an amorphous black pp. by passing H_2S into a solution of Co_2O_3 in acetic acid, or by adding NH_4 sulphide to the solution of a roseo- or purpureo-cobalt salt. Insoluble in KCNAq, thus differing from NiS.

III. Cobalt disulphide CoS_2. (*Cobalt persulphide.*) *Cobalt-glance* is approximately pure $CoS_2.CoAs_2$. Obtained by moderately heating a mixture of 1 part dry CoO with 3 parts S, or of 1 part $CoCO_3$ with $1\frac{1}{2}$ parts S, until excess of S has been removed (Setterberg, *P.* 7, 40). A black lustrous powder; heated in absence of air to redness forms CoS; unacted on by acids except conc. HNO_3 and *aqua regia*.

IV. Cobalto-cobaltic sulphide Co_3S_4. Occurs native as *Linnæite*. Formed, as a greenish-black powder, by heating $CoCl_2Aq$ with K polysulphide solution to 160° (Sénarmont, *A. Ch.* [3] 30, 137).

V. The sulphide Co_4S_3 is said to be obtained by heating $CoSO_4$ to whiteness in a carbon crucible, or by strongly heating Co with S, or CoO with H_2S (Hjortdahl, *C. R.* 65, 75). A grey metal-like, lustrous mass, soluble in hot HClAq with evolution of H_2S.

Cobalt, sulphocyanide of, $Co(SCy)_2$; *v.* Sulphocyanides, under Cyanides.

Cobalt, borotungstate of; *v.* Borotungstates, under Tungsten. M. M. P. M.

COBALTAMINES. (*Cobaltammonium compounds. Cobalt-ammonia compounds. Ammonio-cobalt salts. Ammoniacal cobalt bases.*) Compounds of ammonia, cobalt, and negative radicles, formed either by combination of NH_3 with cobaltous salts in absence of air, or by reactions between cobaltous salts and ammonia in presence of air.

Bergmann noticed the solubility of cobalt salts in ammonia. Tassaert (*A. Ch.* [1] 28, 95, [1799]) noted that colour-changes occur when these solutions stand in the air. Thénard (*A. Ch.* [1] 42, 211 [1803]) and Proust (*A. Ch.* [1] 60, 264 [1806]) explained these changes as caused by absorption of oxygen from the air. Quantitative measurements of the changes in question were made by L. Gmelin (*S.* 36, 236) Pfaff (*S.* 35, 486), Dingler (*B. J.* 10, 139), Hess (*P.* 26, 547), and Winkelblech (*A.* 13, 259). Beetz (*P.* 61, 489; *B. J.* 25, 169) and H. Rose (*P.* 20, 147) carried further the investigation of the compounds produced. In 1850 60 Gibbs (*P. Am. A.*; *v. post*) began his investigations of the compounds formed when ammoniacal solutions of cobalt salts are exposed to air; these researches form the basis of our knowledge of the subject. The chemists who have chiefly contributed to the elucidation of the subject of ammonio-cobalt salts, besides Gibbs, are Fremy, Claudet, Genth, Braun, Mills, Vortmann, F. Rose, and Jorgensen (references will be given to original memoirs by these and other chemists under the individual compounds).

Some cobaltous salts combine with ammonia in absence of air, forming salts which crystallise from ammoniacal solutions but are decomposed by water; these *ammonio-cobaltous salts*, or *cobalto-amines*, generally belong to the form $M.6NH_3$ where M = a cobaltous compound, *e.g.* $CoCl_2$ or $CoSO_4$. Many cobaltous salts in solution react with ammonia in presence of air to form compounds of the type $Co_2X_6.xNH_3$ where X = an acidic radicle. These *ammonio-cobaltic-salts*, or *cobalti-amines*, may be classified, primarily, according to the value of x in the general formula $Co_2X_6.xNH_3$, and secondarily according to the nature and relation to the rest of the salt of the acidic radicle X.

Recent researches have shown that when ammonia is added to a cobaltous salt solution in presence of air, the cobaltous compound probably oxidises, and at the same time combines with ammonia, and that the various ammonio-cobaltic compounds subsequently produced are derived from these oxidised compounds by removal of oxygen and ammonia, followed in some cases by recombination with more ammonia. The final production of this or that ammonio- compound seems to depend chiefly on the relative masses of the cobaltous salt and ammonia or ammonium compound originally present.

The cobaltamines form compounds with many acids and with metallic salts. The mutual relations of the various classes of cobaltamines, and the constitution of each class, are not yet thoroughly elucidated. The following classification is a fairly satisfactory scheme of arrangement, and is generally adopted:—

I. COBALTO-AMINES or AMMONIO-COBALTOUS SALTS. Formed by the reaction of cobaltous salts in solution with ammonia in absence of air. These compounds belong to the form $M.xNH_3$ where M = a cobaltous compound and x is generally = 6.

II. OXY-COBALTAMINES or AMMONIO-OXYCOBALTIC SALTS. Formed by prolonged oxidation of ammoniacal solutions of cobalt salts by a stream of air. Most of these compounds may be represented as belonging to one or other of the series $Co_2(NH_3)_{10}R_4.OH.O.OH$ and $Co_2(NH_3)_{10}R_5.O.OH$, where R = an acidic radicle Cl, Br, I, $\frac{SO_4}{2}$, $\frac{2}{3}PO_4$, &c.

III. COBALTI-AMINES or AMMONIO-COBALTIC SALTS. Formed by exposing ammo niacal solutions of cobaltous salts to the air, and adding an acid or a salt. These compounds may be divided into four main series:—

(i.) HEXAMINES or HEXAMMONIO-COBALTIC SALTS; $Co_2(NH_3)_6R^I_6$ *e.g.* $Co_2(NH_3)_6(SO_4)_3.6H_2O$. These salts are also called *dichrocobaltic salts.*

(ii.) OCTAMINES or OCTAMMONIO-COBALTIC SALTS; $Co_2(NH_3)_8R^I_6$ *e.g.* $Co_2(NH_3)_8Cl_6.2H_2O$.

(iii.) DECAMINES or DECAMMONIO-COBALTIC SALTS; $Co_2(NH_3)_{10}R^I_6$ *e.g.* $Co_2(NH_3)_{10}(OH)_6$.

(iv.) DODECAMINES or DODECAMMONIO-COBALTIC SALTS; $Co_2(NH_3)_{12}R^I_6$ *e.g.* $Co_2(NH_3)_{12}(CO_3)_3.7H_2O$. The fourth series is also called the series of *luteo-cobaltamines* or *luteo-ammonio-cobaltic salts.*

The *octamines* and *decamines* are generally divided each into three divisions:—

OCTAMINES.

(*a*) *Praseo-cobaltic salts*; normal salts, *e.g.* $Co_2(NH_3)_8(SO_4)_3.4H_2O$.

(*b*) *Fusco-cobaltic salts*; basic salts, *e.g.* $Co_2(NH_3)_8Cl_4(OH)_2.2H_2O$.

(*c*) *Croceo-cobaltic salts,* also called *nitramines of the octamine series*; derived from praseo-salts by replacing $\frac{2}{3}$ of R by NO_2 *e.g.* $Co_2(NH_3)_8SO_4(NO_2)_4$.

DECAMINES.

(*a*) *Roseo-cobaltic salts*; $Co_2(NH_3)_{10}Cl_6.2H_2O$

(*b*) *Purpureo-cobaltic salts*; $Co_2(NH_3)_{10}Cl_6$.

} differ in quantity of H_2O they contain.

(*c*) *Xantho-cobaltic salts,* also called *nitramines of the decamine series*; derived from purpureo- or roseo-salts by replacing $\frac{1}{3}$ of R by NO_2 *e.g.* $Co_2(NH_3)_{10}Cl_4(NO_2)_2.2H_2O$.

Many cobaltamines of different classes combine with acids and with metallic salts to form double compounds.

The empirical formulæ given to the cobaltamines do not sufficiently represent the properties of these compounds. It is sometimes necessary to distinguish between the functions of different radicles in the same compound; and isomerism is exhibited by some of these bodies. Thus, in the octamine series, two octamine chlorides exist, $Co_2(NH_3)_8Cl_6.2H_2O$; one is green, it loses all its water at 100°, its aqueous solution is easily decomposed giving a pp. of $Co_2O_3.3H_2O$; when the solution of this salt is treated with fairly conc. HClAq a violet salt crystallises out, having the same composition as the green salt; this violet salt does not begin to lose water at 120°, it is considerably more stable than the green salt. These two salts are representatives of two subdivisions of the division *praseo-salts*; the subdivisions are known as *octamine-praseo-salts* and *octamine-purpureo-salts* respectively. Again, in the decamine series; the chloride $Co_2(NH_3)_{10}Cl_6$ is a violet-red solid which dissolves in water, and when digested with dilute HClAq yields a red dichroïc powder having the composition $Co_2(NH_3)_{10}Cl_6.2H_2O$; this salt is very unstable, it is changed to the violet-red compound on warming or on solution in water; a solution of this salt is not ppd. by $Na_4P_2O_7Aq$, while a solution of the violet-red salt is ppd. by this reagent. These two salts are representatives of two divisions of the DECAMINE SERIES, viz. the *purpureo-* and *roseo-decamines.* Some of the purpureo-salts crystallise with xH_2O, *e.g.* $Co_2(NH_3)_{10}(SO_4)_3.H_2O$; but such salts lose water without undergoing essential change, hence the water is water of crystallisation, whereas in the roseo-salts the water seems to be rather water of constitution. Again, there is a compound of the purpureo-division of the decamine series, $Co_2(NH_3)_{10}(SO_4)_2(NO_3)_2$, which is isomeric with another compound of the same division, and both are isomeric with a roseo-salt of the decamine series. So also in one of the series of oxycobaltamines, viz. the series $Co_2(NH_3)_{10}R_5.O.OH$, $\frac{4}{5}$ of the radicle R are more firmly held to the rest of the salt than the remaining one-fifth.

It is generally possible to give formulæ to each series, or division, which shall more or less satisfactorily represent the typical reactions of the compounds as connected with the arrangement of the different radicles, and ammonia, relatively to the cobalt atoms; but, considering the present state of knowledge of the constitution of complex mineral compounds, such formulæ have little permanent value.

In this article accounts will be given of the leading properties of each class, series, and division, of the ammonio-cobalt compounds, and descriptions will be added of the methods of preparation of one or two of the best-known members of each group; the less-known compounds will merely be recorded. For details concerning individual compounds other than those described, reference must be made to the original memoirs. (A good account of the cobaltamines will be found in the article '*Kobalt*' in Ladenburg's *Handwörterbuch der Chemie*, 5, 601 *et seq.*)

Class I.—COBALTO-AMINES or AMMONIO-COBALTOUS SALTS, $M.xNH_3$; M = cobaltous salt, x generally = 6. These salts were first examined by H. Rose (*P.* 20, 147). They are produced by combination of NH_3 with dry cobaltous salts, or adding conc. NH_3Aq to conc. solutions of cobaltous salts in absence of air; they are decomposed by heat with loss of NH_3; their aqueous solutions also undergo decomposition, especially on warming.

Ammonio-cobaltous chloride $CoCl_2.6NH_3$; obtained by adding conc. NH_3Aq to conc. $CoCl_2Aq$ until the blue pp. which forms is dissolved, in absence of air, and allowing to crystallise. Red octahedra; unchanged in a closed vessel; in the air, or over H_2SO_4, or by warming with Aq, NH_3 is separated. Soluble, without change, in dilute NH_3Aq, scarcely sol. in conc. NH_3Aq, insol. alcohol. The compound $CoCl_2.4NH_3$ is formed when NH_3 is absorbed by dry $CoCl_2$; and $CoCl_2.2NH_3$ is produced by heating $CoCl_2.6NH_3$ to 120° (H. Rose, *P.* 20, 147).

Ammonio-cobaltous nitrate $Co(NO_3)_2.6NH_3.2H_2O$; obtained similarly to the chloride. Red crystals, which quickly turn brown; decomposed by water with removal of NH_3 (Fremy, *A. Ch.* [3] 35, 257).

Ammonio-cobaltous sulphate $CoSO_4.6NH_3$; obtained by adding alcohol to an ammoniacal solution of $CoSO_4$ (Fremy), or by combination of dry $CoSO_4$ with NH_3 (Rose).

The compounds $CoBr_2.6NH_3$, $CoI_2.6NH_3$, and $CoI_2.4NH_3$ are also known (Rammelsberg, *P.* 55, 245; 48, 155).

Class II.—OXY-COBALTAMINES or AMMONIO-OXYCOBALTIC SALTS, or OXYCOBALTIAC SALTS, $Co_2(NH_3)_{10}R^I_4.OH.O.OH$, and $Co_2(NH_3)_{10}R^I_5.O.OH$, where R^I = monovalent acidic radicle. These salts are obtained by the combined action of NH_3 and air on cobaltous salts; when a stream of air is passed into an ammoniacal solution of a cobaltous salt, the colour of the liquid changes to brown, and if the solution is sufficiently conc. the oxycobaltamine frequently separates; in some cases the salt is obtained by adding a salt or an acid to the solution obtained as described. The oxycobaltamines generally partially decompose when heated alone or in NH_3Aq, giving off oxygen and forming salts of the octamine (*fusco-*) series, which, by combination with NH_3, form salts of decamine and dodecamine series. The oxycobaltamines are decomposed by warm water with ppn. of $Co_2O_3.3H_2O$ or a basic cobaltous salt and evolution of oxygen. Dilute acids partially decompose the oxycobaltamines of the form $Co_2(NH_3)_{10}R_4.OH.O.OH$ with production of green salts and separation of water. The green salts thus formed are regarded by Vortmann (*M.* 6, 401) as *anhydro-oxycobaltamines*; *e.g.* oxycobaltamine chloride $Co_2(NH_3)_{10}Cl_4.OH.O.OH$ with conc. HClAq gives anhydro-oxycobaltamine chloride $Co_2(NH_3)_{10}Cl_4.Cl.O.OH$, thus

$$Co_2(NH_3)_{10}Cl_4.OH.O.OH + HCl$$
$$= Co_2(NH_3)_{10}Cl_4.Cl.O.OH + H_2O.$$

The oxycobaltamines were formerly represented as containing the group Co_2O_2; and the anhydro-oxycobaltamines were regarded as acid salts derived from the oxycobaltamines (Maquenne, *C. R.* 96, 344): the change from the chloride to the anhydrochloride, for instance, was formulated thus:—

$$Co_2O_2(NH_3)_{10}Cl_4.H_2O + HCl$$
$$= Co_2O_2(NH_3)_{10}Cl_4.ClH + H_2O.$$

But Vortmann's observation that solutions of the oxycobaltamines reduce $KMnO_4Aq$ and $K_2Cr_2O_7Aq$ points to the presence of the group O.OH; and the formation of octamine salts with evolution of ammonia and oxygen by heating ammoniacal solutions of oxycobaltamines confirms this supposition; thus

$$Co_2(NH_3)_{10}(NO_3)_4.OH.O.OH.H_2O$$
$$= Co_2(NH_3)_8(NO_3)_4(OH)_2 + 2NH_3 + H_2O + O.$$

Whether the green salts obtained by the reaction of acids with the oxycobaltamines are regarded as acid salts of the oxycobaltamines (Maquenne), or as anhydro-oxycobaltamines (Vortmann), in either case $\frac{1}{5}$ of the acid radicle is represented as related to the rest of the salt differently from the other four-fifths; thus the nitrate is either $Co_2(NH_3)_{10}(NO_3)_4.NO_2.O.OH$ or $Co_2O_2(NH_3)_{10}.(NO_3)_4.NO_3H$. If Vortmann's formula for the oxycobaltamines is adopted, it is better to regard the green salts as anhydro-oxycobaltamines. One-fifth of the acid radicle is regarded by Vortmann as directly associated with the Co atom. The existence of acid salts of the oxycobaltamines, differing in properties from the anhydro-oxycobaltamines, and very probably belonging to the same type as the oxycobaltamines (*e.g.* $Co_2(NH_3)_{10}(NO_3)_4.OH.O.OH.HNO_3$), tends to show that the green salts are better regarded as anhydro-oxycobaltamines than as acid salts of oxycobaltamines.

Series I. **Oxy-cobaltiac salts, or Ammonio-oxy-cobaltic salts,** $Co_2(NH_3)_{10}R^I_4.OH.O.OH$.

Oxy-cobaltamine iodide $Co_2(NH_3)_{10}I_4.OH.O.OH$ (Vortmann, *M.* 6, 404); obtained by adding cold conc. KIAq to an oxidised ammoniacal solution of $CoCl_2$. Green needles; unchanged in air; decomposed by much H_2O with evolution of O. Dilute acids separate I and evolve O; hot conc. HNO_3 forms luteo-cobalt nitrate $Co_2(NH_3)_{12}(NO_3)_6$.

Oxy-cobaltamine chloride $Co_2(NH_3)_{10}Cl_4.OH.O.OH$ (Vortmann, *M.* 6, 401); obtained by dissolving crystals of $CoCl_2$ in $2\frac{1}{2}$ parts NH_3Aq S.G. ·912, with gentle warming, passing air into the cold solution until the pp. of $CoCl_2.xNH_3$, which forms, redissolves, saturating with NH_4Cl, and adding alcohol; ppn. is aided by rubbing with a glass rod. Greenish-brown powder; very unstable, easily giving off O, and then passing into fusco-cobalt chloride $Co_2(NH_3)_8.Cl_4(OH)_2$ (*cf.* Fremy, *A. Ch.* [3] 35, 257).

Oxy-cobaltamine nitrate $Co_2(NH_3)_{10}(NO_3)_4.OH.O.OH$ (Fremy, *l.c.*; Vortmann, *l.c.*; Gibbs, *P. Am. A.* 10 [1875] 1; 11, 1); obtained by leading air into saturated $Co2NO_3Aq$, to which saturated NH_4NO_3Aq, and 5 parts of NH_3Aq S.G. ·938, have been added. Dark brown prismatic crystals. Very unstable; loses water and a little NH_3 in dry air; when heated appears to form fusco-cobalt nitrate $Co_2(NH_3)_8(NO_3)_4(OH)_2$.

Oxy-cobaltamine sulphate $Co_2(NH_3)_{10}(SO_4)_2.OH.O.OH$ (Fremy; Vortmann); obtained similarly to, but more easily than, the nitrate. Dark brown crystals; more stable than the nitrate; heated to 110°–120° it loses H_2O, NH_3, and O, and forms fusco-cobalt sulphate $Co_2(NH_3)_8(SO_4)_2(OH)_2$.

Oxy-cobaltamine acid nitrate, sulphate, sulphato-chloride, &c. These salts are obtained by dissolving the nitrate or sulphate in conc. HNO_3 or H_2SO_4 respectively, or by dissolving the sulphate or nitrate in conc. HClAq. Their compositions are expressed by the formulæ

$$Co_2(NH_3)_{10}(NO_3)_4.OH.O.OH.HNO_3,$$
$$Co_2(NH_3)_{10}(SO_4)_2.OH.O.OH.2H_2SO_4,$$
$$Co_2(NH_3)_{10}(SO_4)Cl_2.OH.O.OH.4HCl,$$
$$Co_2(NH_3)_{10}(NO_3)_2Cl_2.OH.O.OH.4HCl,$$
$$\text{and}\quad Co_2(NH_3)_{10}(SO_4)(NO_3)_2.OH.O.OH.4HNO_3.$$

These salts are all very easily decomposed by heat, giving green salts, the change probably consisting in removal of the excess of acid.

Series II. **Anhydro-oxycobaltiac salts, or Anhydro-oxy-cobaltamines,** $Co_2(NH_3)_{10}R^I_4.R^I.O.OH$ (Vortmann, *M.* 6, 404).

Anhydro-oxy-cobaltamine chloride $Co_2(NH_3)_{10}Cl_4.Cl.O.OH.H_2O$; obtained by digesting freshly prepared oxy-cobaltamine chloride in cold conc. HClAq until the colour is green, and crystallising from warm dilute HClAq. Small green needles; stable in air; loses NH_3 and H_2O on warming; e. sol. water, the solution rapidly decomposes; when a solution in HClAq is boiled, purpureo-chloride, $Co_2(NH_3)_{10}Cl_6$, is formed; heated with NH_3Aq, purpureo-chloride is formed, along with luteo-chloride $Co_2(NH_3)_{12}Cl_6$. Forms double salts with $2PtCl_4.5H_2O$, and $3HgCl_2$.

Anhydro-oxy-cobaltamine nitrate $Co_2(NH_3)_{10}(NO_3)_4NO_3.O.OH.H_2O$; obtained by adding oxy-cobaltamine nitrate to a mixture of equal vols. conc. HNO_3 and H_2O, digesting in the cold and then warming until all is dissolved; on cooling a blue-green finely crystalline pp. forms. Sl. sol. water, solution rapidly decomposes; solution in dilute acids may be boiled without change.

The other important salts of the *anhydro-oxy-cobaltamine series* are the following: --

Sulphate $(Co_2(NH_3)_{10}.O.OH)_2(SO_4)_5.8H_2O$.

Dichromate $(Co_2(NH_3)_{10}.O.OH)_2(Cr_2O_7)_5.8H_2O$.

Chloronitrates
$Co_2(NH_3)_{10}(NO_3)_2Cl_2.Cl.O.OH.H_2O$, and
$Co_2(NH_3)_{10}(NO_3)_4Cl.O.OH.H_2O$.

Acid sulphates
$(Co_2(NH_3)_{10}.O.OH)_2(SO_4)_5.xH_2SO_4.nH_2O$; $x = 1$ and 2, and $n = 2$ and 3.

Acid nitrato-sulphate
$Co_2(NH_3)_{10}(SO_4)_2(NO_3).O.OH.H_2SO_4.H_2O$.

Class III.—COBALTI-AMINES, or AMMONIO-COBALTIC SALTS $Co_2(NH_3)_xR^I_6$; $x = 6$, 8, 10, 12. This class comprises by far the greater number of the ammonio-cobalt salts. It is divided into four series, and some of these are again subdivided. The series are:

(i.) *Hexamines* $Co_2(NH_3)_6R_6$.
(ii.) *Octamines* $Co_2(NH_3)_8R_6$.
(iii.) *Decamines* $Co_2(NH_3)_{10}R_6$.
(iv.) *Dodecamines* $Co_2(NH_3)_{12}R_6$.

Series I. HEXAMINES, or HEXAMMONIO-COBALTIC SALTS $Co_2(NH_3)_6R^I_6$. Also called *dichro-cobaltic salts*. These salts are very unstable; they are readily decomposed by potash.

Hexamine chloride $Co_2(NH_3)_6Cl_6.H_2O$ (*Dichrocobaltic-chloride*). Octamine cobalt carbonate, $Co_2(NH_3)_8(CO_3)_3$, is obtained by dissolving $CoCO_3$ in NH_3Aq in presence of $(NH_4)_2CO_3$, exposing to air for some time, evaporating on water-bath to a small volume, adding $(NH_4)_2CO_3$ and evaporating again; this salt is dissolved in NH_3Aq, $(NH_4)_2CO_3$ is added, and the solution is evaporated to dryness on the water-bath; evaporation after addition of a little water and $(NH_4)_2CO_3$ is repeated two or three times; the crude carbonate thus obtained is treated with dilute HClAq; the turbid liquid is heated nearly to boiling, and then quickly cooled, when the hexamine chloride separates as small green crystals (Vortmann, *B.* 10, 1451; 15, 1890). Crystallises from neutral solution in green crystals, appearing almost black when large; crystallises from acidified solution in red-brown tables. Dichroïsm is best seen by evaporating a drop of solution of salt on an object-glass, and examining under microscope. Water is not completely removed at 120°. Fairly soluble in water; on warming solution becomes violet, and contains octamine purpureo-chloride $Co_2(NH_3)_8Cl_6.2H_2O$ which may be ppd. by HCl; solution in HClAq on warming gives pp. of decamine purpureo-chloride $Co_2(NH_3)_{10}Cl_6$. Forms a double salt with $HgCl_2$.

The chief salts of the *hexamine series*, besides the chloride, are the following: $M = Co_2(NH_3)_6$.

Basic carbonate $M.(OH)_2(CO_3)_2.3H_2O$.

Nitrates $M.(NO_3)_6.8H_2O$; and $M.(NO_3)_3(OH)_3.2H_2O$.

Sulphate $M.(SO_4)_3.6H_2O$.

Nitrite $M.(NO_2)_6$ (Erdmann, *J. pr.* 97, 405).

Series II. OCTAMINES, or OCTAMMONIO-COBALTIC SALTS $Co_2(NH_3)_8R^I_6$. The salts of this series are arranged in three divisions, the *praseo-*, the *fusco-*, and the *croceo- cobaltic salts*.

Division I. *Praseo-cobaltic salts.*

Praseo-cobaltic chloride $Co_2(NH_3)_8Cl_6.2H_2O$ (Vortmann, *B.* 10, 1451; 15, 1890; F. Rose, *Untersuchungen über ammoniakalische Kobaltverbindungen* [Heidelberg, 1871]). This salt exists in two modifications generally known as *praseo-cobaltic chloride* and *octamine-purpureo-cobalt chloride*, respectively. Praseo-chloride forms green lustrous crystals; e. sol. water, the solution readily decomposes, turning violet, and HCl then pps. decamine-purpureo-chloride $Co_2(NH_3)_{10}Cl_6.2H_2O$; dried at 100° this salt becomes anhydrous. Octamine-purpureo-chloride forms deep violet octahedra; does not lose any H_2O at 120°.

The praseo-salt is generally found in the mother-liquor when any cobalt salt is exposed to air in presence of ammonia, and the solution is ppd. by HCl; it is separated from such liquid by addition of NH_4Cl. The pp. is separated from admixed decamine-purpureo-chloride by washing with alcohol, drying, dissolving in conc. H_2SO_4, and carefully ppg. by HClAq added drop by drop; it is then dissolved in ice-cold water, and at once ppd. by a little HClAq.

The purpureo-salt is obtained by oxidising an ammoniacal cobalt chloride solution in the air, evaporating to a small bulk after addition of $(NH_4)_2CO_3$, filtering from ppd. luteo-chloride $(Co_2(NH_3)_{12}Cl_6)$ and allowing to stand.

When a praseo-chloride solution is warmed with fairly dilute HClAq, a violet liquid is obtained, from which octamine-purpureo-chloride separates on cooling. When conc. H_2SO_4 is added to an aqueous solution of the purpureo-chloride crystals of the praseo-salt gradually separate.

Praseo-chloride forms two double salts with $HgCl_2$, viz., $M.HgCl_2$ and $M.2HgCl_2$. Purpureo-chloride forms the double salts $M.6HgCl_2.2H_2O$ and $M.3HgCl_2.H_2O$; where $M = Co_2(NH_3)_8Cl_6$. When a solution of octamine carbonate, formed as described under *hexamine chloride* (*v. supra*), is ppd. by *cold* HClAq, small red crystals are obtained; these have the composition $Co_2(NH_3)_8Cl_6.2H_2O.2H_2O$; at 120° the crystals lose $2H_2O$, becoming octamine purpureo-chloride. This salt is usually known as octamine roseo-cobalt chloride; it forms a double salt $Co_2(NH_3)_8Cl_6.2H_2O.6HgCl_2.3H_2O$.

The two salts, praseo-cobalt chloride and octamine-purpureo-chloride, are isomeric; in the second the two molecules of water are more firmly held to the rest of the salt than in the praseo- compound. The roseo-chloride differs from the two others by containing two molecules of water loosely held to the rest of the salt. Each of these salts is the representative of a subdivision of praseo-cobaltic salts; the *praseo-salts proper*, the *octamine purpureo-salts*, and the *octamine roseo-salts*. The chief salts in these subdivisions are the following:— $M = Co_2(NH_3)_8$.

Praseo-cobalt chromato-chloride $M.Cl_4.Cr_2O_7.H_2O$.

Praseo-cobalt nitrato-chloride $M.Cl_4.(NO_3)_2.2H_2O$.

Octamine purpureo-cobalt chromate $M.(CrO_4)_3.2H_2O.2H_2O$.

Octamine-purpureo-cobalt sulphate $M.(SO_4)_3.2H_2O.2H_2O$.

Octamine roseo-cobalt sulphate $M.(SO_4)_3.2H_2O.4H_2O$.

Octamine cobalt carbonates $M.(CO_3)_3.3H_2O$; and $M.(CO_3)_3.H_2CO_3.2H_2O$.

Octamine cobalt sulphato-carbonate $M.(CO_3)_2SO_4.3H_2O$.

Octamine cobalt nitrate $M.(NO_3)_6.2H_2O$.

Division II. *Fusco-cobaltic salts* (Fromy, *A. Ch.* [3] 35, 257). These compounds, which are basic salts of the octamine series, are obtained from the brown liquids formed by allowing ammoniacal cobalt solutions to stand for a long time in air; they are also formed by decomposing oxy-cobaltamines by water. They are non-crystallisable; alcohol, or passage of an ammonia-stream, pps. them from their solutions. Boiled with water, especially if alkali is present, they are decomposed with separation of $Co_2O_3.3H_2O$. The chief salts are the following: $M = Co_2(NH_3)_8(OH)_2$.

Fusco-cobalt chloride $M.Cl_4.2H_2O$.

Fusco-cobalt nitrate $M.(NO_3)_4.2H_2O$.

Fusco-cobalt sulphate $M.(SO_4)_2.2H_2O$.

Division III. *Croceo-cobaltic salts.* These compounds, which are tetra-nitro-derivatives of the praseo-salts, are produced by the action of ammonia and nitrous acid (or ammonium or potassium nitrite) on solution of $Co2NO_3$ or $CoSO_4$; dark-coloured solutions are thus formed, from which the croceo-salts separate in yellow crystals mixed with $Co(OH)_2$.

Croceo-cobaltic sulphate $Co_2(NH_3)_8(NO_2)_4.SO_4$. Prepared by adding NH_3Aq and $(NH_4)NO_2$ to $CoSO_4Aq$, and recrystallising from hot dilute H_2SO_4Aq. Yellow lustrous tables; large wine-red crystals from dilute solutions. Sl. sol. hot or cold water. The other important croceo-salts are represented by the following formulæ, where $M = Co_2(NH_3)_8(NO_2)_4$: *Chloride* $M.Cl_2$; forms double salts $M.Cl_2.PtCl_4$ and $M.Cl_2.2AuCl_3$; *Bromide* $M.Br_2$; *Chromate* $M.CrO_4$; *Dichromate* $M.Cr_2O_7$; *Nitrate* $M.(NO_3)_2$; *Periodide* $M.I_2.I_4$.

Series III. DECAMINES, or DECAMMONIO-COBALTIC SALTS, $CO_2(NH_3)_{10}R^I_6$. This series contains very many compounds; these compounds are well-marked and stable bodies, frequently obtained from cobaltamines by decomposing these by acids. The series is arranged in three divisions: the roseo-, the purpureo-, and the xantho-salts. The following are typical representatives of these divisions: *roseo-cobaltic chloride* $Co_2(NH_3)_{10}Cl_6(H_2O)_2$; *purpureo-cobaltic chloride* $Co_2(NH_3)_{10}Cl_6$; *xantho-cobaltic chloride* $Co_2(NH_3)_{10}(NO_2)_2Cl_4$. The roseo- and purpureo-salts differ in the quantities of water they contain, the purpureo-salts are generally anhydrous, the roseo-salts usually contain $2H_2O$; inasmuch as these salts form very distinct compounds with different properties, it seems necessary to conclude that the $2H_2O$ of the roseo-salts is not water of crystallisation, but forms an integral part of the molecule of each of these salts. The purpureo-salts are less soluble in water than the roseo-salts; they are changed to the latter by long-continued warming in presence of water, by long-continued digestion with dilute acids at the ordinary temperature, or generally by processes which result in hydration, but not merely by solution in water and crystallisation. The xantho-salts bear a somewhat similar relation to the purpureo-salts that the croceo-compounds of the octamine series bear to the praseo-compounds of the same series; the xantho-salts are dinitro-derivatives of the purpureo-salts, the croceo-salts are tetra-nitro-derivatives of the praseo-salts.

Division I. *Roseo-cobaltic salts.* These salts are obtained as products of the decomposition of the oxy-cobaltamines, from aqueous solutions of which they are ppd. by acids in the cold. They are obtained from purpureo-salts by long-continued digestion with dilute acids, or, more readily, by treating these salts with alkalis, *e.g.* dilute solution of NH_3 or $NaOH$, Ag_2O and water, or $BaCO_3$—and subsequent saturation with acids. The roseo-salts form red to peach-coloured crystals, which exhibit dichroism; they are fairly easily soluble in water; their ammoniacal solutions are decomposed on boiling with ppn. of $Co_2O_3.3H_2O$. These salts lose water by treatment with conc. acids, and form purpureo-salts. Roseo-salts in solution give a pp. of roseo-pyrophosphate on addition of sodium pyrophosphate; potassium ferrocyanide also gives a pp. with these salts; these reactions serve to distinguish roseo- from purpureo-salts (Jörgensen, *J. pr.* [2] 31, 49). The roseo-salts show many analogies—*e.g.* in crystalline form, methods of formation, and general reactions—with the dodecammonio- (or luteo-) salts $Co_2(NH_3)_{12}R^I_6$. Jörgensen (*J. pr.* [2] 31, 49) regards the roseo-decamines as luteo-salts in which $2NH_3$ is replaced by $2H_2O$. Roseo-chloride, nitrate, oxalate, &c., in aqueous solutions react with $BaCl_2Aq$ and $Ba(NO_3)_2Aq$ to give only roseo-salts. Roseo-chloride is soluble in 4·8 pts. water at 10°, while purpureo-chloride requires 287 pts. water for solution at 10°. Aqueous solutions of the two chlorides often give different compounds by reacting with the same re-agents, *e.g.*:

With $PtCl_4$,	*roseo-chloride* gives	$M.Cl_6.2PtCl_4.5H_2O$;	and *purpureo-chloride* gives	$M.Cl_6.2PtCl_4$.
„ $AuCl_3$	„ „	$M.Cl_6.2AuCl_3.2H_2O$;	„ „	„ $M.Cl_6.2AuCl_3$.
„ $(NH_4)_2C_2O_4$	„ „	$M.(C_2O_4)_3.6H_2O$;	„ „	„ $M.Cl_2(C_2O_4)_2$.

$M = Co_2(NH_3)_{10}$.

Roseo-cobaltic chloride $Co_2(NH_3)_{10}(H_2O)_2Cl_6$ (Jörgensen, *J. pr.* [2] 18, 209; 31, 49; Gibbs a. Genth, *Researches on the Ammonia-cobalt bases* [Washington, 1856]; Mills, *P. M.* [4] 35, 245; Geuther, *Lehrbuch der Chemie*, 442). Obtained from an ammoniacal solution of $CoCl_2$ by oxidising in air, or by $KMnO_4Aq$ (Mills), and ppg. by HCl, avoiding rise of temperature; also by digesting purpureo-chloride (*q. v.*) with dilute $HClAq$, or by dissolving the same salt in NH_3Aq and ppg. by HCl in the cold (Jörgensen, *l.c.*; Geuther, *l.c.*). A red, dichroic powder, appearing crystalline under the microscope. Loses $2H_2O$ at 100°, giving purpureo-chloride. Soluble in 4·8 pts. water at 10°. Very unstable, easily going to purpureo-chloride. Forms a gold salt, $M.2AuCl_3$, by reaction with $AuCl_3NaCl$: forms three Pt salts; $M.PtCl_4.2H_2O$, $M.2PtCl_4,H_2O$, and $M.3PtCl_2.6H_2O$

(Jörgensen, *l.c.*): forms two Hg salts; $M.2HgCl_2$ and $M.6HgCl_2.2H_2O$ (Jörgensen, *l.c.*).

[$M = CO_2(NH_3)_{10}(OH_2)_2Cl_6$.]

Gibbs (*l.c.*) describes a *yellow form of roseo-chloride* obtained by decomposing the yellow form of roseo-sulphate (*q. v.*) by $BaCl_2Aq$; this form does not yield purpureo-chloride by reaction with HClAq.

Roseo-cobaltic sulphate $Co_2(NH_3)_{10}(H_2O)_2(SO_4)_3.3H_2O$ (Fremy, *A. Ch.* [3] 35, 257; Gibbs a. Genth, *Researches on the Ammonia-cobalt bases* [Washington, 1856]; Gibbs, *P. Am. A.* 10, 1; 11, 1; Braun, *A.* 138, 109; 142, 50; Jörgensen, *J. pr.* [2] 31, 49; 35, 417). Obtained by adding the proper quantity of H_2SO_4Aq to a solution of roseo-carbonate, and evaporating over H_2SO_4, or ppg. by alcohol; the roseo-carbonate solution is prepared by decomposing purpureo-chloride or bromide by Ag_2CO_3 (Genth, *A.* 80, 275; Claudet, *P. M.* [4] 2, 253; Jorgensen, *J. pr.* [2] 18, 209; 19, 49). Roseo-sulphate forms reddish crystals; soluble in 91·6 pts. water at 17°, and in 58 pts. water at 27°. Two other forms of the sulphate are described by Gibbs a. Genth (*P. Am. A.* 10, 1; 11, 1); they differ chiefly in solubility from the ordinary form. An *acid roseo-sulphate* $Co_2(NH_3)_{10}(OH)_2(SO_4)_3.2H_2SO_4.H_2O$ is described by Fremy (*l.c.*) (*v.* also Jorgensen, *l.c.*). The normal sulphate forms a gold and also a Pt salt: $M.(SO_4)_2Cl_2.2AuCl_3$ and $M.(SO_4)_2Cl_2.PtCl_4$ (Jörgensen, *l.c.*) [$M = Co_2(NH_3)_{10}(OH_2)_2$].

The chief salts of the roseo- division besides the chloride and sulphate are represented by the following formulæ, where $M = Co_2(NH_3)_{10}(H_2O)_2$:— *Dichromate*, $M.(Cr_2O_7)_3.3H_2O$ (Gibbs). *Bromide*, $M.Br_6$ forming Pt salts with $2PtBr_4.2H_2O$, and $3PtBr_4.4H_2O$ (Jorgensen). *Iodide*, $M.I_6$ (Jörgensen). *Nitrate*, $M.(NO_3)_6$ (Gibbs; Jorgensen); forming a Pt salt, $M(NO_3)_2Cl_4.2PtCl_4.2H_2O$. *Nitrato-sulphate*, $M.(NO_3)_2(SO_4)_2$ (J.). *Oxalate*, $M.(C_2O_4)_3.4H_2O$. *Sulphato-oxalate*, $M.(C_2O_4)_2(SO_4).SO_4.2H_2O$ (Gibbs a. Genth). *Orthophosphates*, $M.(PO_4)_2.H_3PO_4.4H_2O$; $M.(OH)_2(PO_4H)_2.2H_2O$ (J.). *Pyrophosphates*, $M_2.(P_2O_7)_3.12H_2O$; $M.(P_2O_7H)_2$ (J.); also $M.(P_2O_7Na)_2.23H_2O$ (Gibbs, Braun, Porumbaru, *C. R.* 91, 933; 93, 342). *Bromo-sulphate*, $M.Br_2(SO_4)_2$; forms a gold salt $M.Br_2(SO_4)_2.2AuBr_3$ (J.). *Iodosulphate*, $M.I_2(SO_4)_2$ (Krok, *Acta Univers. Lund*, 1870). *Sulphite*, $M.(SO_3)_3.3H_2O$ (Gibbs); forming a double salt $M.(SO_3)_3.Co_2(SO_3)_3.9H_2O$ (Künzel, *J. pr.* 72, 209; Geuther, *l.c.*).

Division II. *Purpureo-cobaltic salts.* $Co_2(NH_3)_{10}R^{I}_{6}$. These salts are the most stable of all the cobaltamines. They are formed from the roseo-salts by heating with conc. acids, or sometimes by continued digestion with conc. acids in the cold; also by the action of acids on fusco- and xantho-cobaltic salts. The purpureo-salts are generally anhydrous; they are less soluble in water than the roseo-salts, into which salts they are changed by prolonged digestion with dilute acids. Solutions of purpureo-salts are decomposed by boiling with alkalis, giving pps. of $Co_2O_3.3H_2O$. These salts probably contain two acidic radicles more closely associated with the rest of the salt than the other four radicles; *e.g.* they form xantho-salts $Co_2(NH_3)_{10}(NO_2)_2R^{I}_{4}$; again, chloro-purpureo-sulphate $Co_2(NH_3)_{10}Cl_2(SO_4)_4$ does not give HCl with conc. H_2SO_4, nor is it ppd. by $AgNO_3Aq$ even on warming (Jörgensen). It is convenient to consider the purpureo-salts in four main sections: the *chloropurpureo-salts* $Co_2(NH_3)_{10}Cl_2.R^{I}_{4}$, the *bromopurpureo-salts* $Co_2(NH_3)_{10}Br_2.R^{I}_{4}$, the *nitrato-purpureo-salts* $Co_2(NH_3)_{10}(NO_3)_2.R^{I}_{4}$, and the *sulphato-purpureo-salts* $Co_2(NH_3)_{10}(SO_4).R^{I}_{4}$.

Chloro-purpureo-cobaltic chloride $Co_2(NH_3)_{10}Cl_2.Cl_4$ (Mills, *P. M.* [4] 35, 245; Porumbaru, *C. R.* 91, 933; 93, 342; Genth, *A.* 80, 275; Claudet, *P. M.* [4] 2, 253; Terreil, *C. R.* 62, 139; Braun, *A.* 138, 109; 142, 50). This salt is formed when an ammoniacal solution of $CoCl_2$ is allowed to oxidise in the air; boiling with excess of HClAq pps. the salt as a carmine-red powder. The reaction of HClAq or NH_4ClAq with very many cobaltamines produces this salt. Instead of oxidising $CoCl_2$ in NH_3Aq in air, which process takes a long time to accomplish, it is advisable to use $KMnO_4Aq$ (Terreil), bleaching powder (Mills), or ozonised turpentine or indigo-blue (Braun). Chloro-purpureo-chloride is a carmine-red crystalline powder; in larger crystals it appears carmine-red to black; these crystals are tetragonal pyramids, isomorphous with roseo-chloride; they are dichroic; S.G. ^{23} 1·802; sol. 287 pts. water at 10·2°, 255 pts. at 11·5°, and 244 pts. at 15·5° (F. Rose); insol. alcohol according to Fremy (*A. Ch.* [3] 35, 257). An aqueous or alkaline, but not an acid, solution, pps. $Co_2O_3.3H_2O$ on boiling. Heated in air $CoCl_2$ and Co are obtained; at a higher temperature with free access of air Co_3O_4 is produced. Many double salts of chloropurpureo-chloride are known, *e.g.* $M.Cl_4.2PtCl_4$; $M.Cl_4.2AuCl_3$; $M.Cl_4.6HgCl_2$; $M(SiF_6)_2$ [$M = Co_2(NH_3)_{10}Cl_2$].

The other chief salts of the *chloropurpureo*-section of purpureo-cobaltic salts are the following:—

$M = Co_2(NH_3)_{10}Cl_2$.

Bromide, $M.Br_4$; double salts, $M.Br_4.2PtBr_4$, $(M.Br_4)_2.9HgBr_2$.

Iodide, $M.I_4$; double salts, $M.I_4.4HgI_2$, $M.I_4.2HgI_2$.

Carbonates, $M.(CO_3)_2.9H_2O$; $M.(CO_3)_2.H_2O$.

Chromate, $M.(CrO_4)_2$ (Jörgensen, *J. pr.* [2] 18, 209).

Dichromate, $M.(Cr_2O_7)_2$ (Jorgensen).

Nitrate, $M.(NO_3)_4$ (J.).

Oxalate, $M.(C_2O_4)_2$ (J.).

Pyrophosphates, $M.(P_2O_7).xH_2O$; $M.(P_2O_7).H_4P_2O_7$ (J.); double salts, $M.(2PO_4H.5MoO_3)$, $M.(2PO_4NH_4.5MoO_3)$ (J.).

Sulphates, $M.(SO_4)_2.4H_2O$; $M.(SO_4)_2$; $M_2.(SO_4).(HSO_4)_6$ (J.).

Dithionate, $M.(S_2O_6)_2$ (J.).

Thiosulphate, $M.(S_2O_3)_2$ (J.).

Tartrate, $M.(C_4H_5O_6)_4.5H_2O$ (J.).

Bromo-purpureo-cobaltic bromide $Co_2(NH_3)_{10}Br_2.Br_4$ (Jörgensen, *J. pr.* [2] 19, 49). Obtained by oxidising ammoniacal $CoBr_2Aq$ and heating with HBrAq; or by heating roseo-sulphate with conc. HBrAq, and in other ways. Blue-violet, dichroic, microscopic octahedra; from solutions in very dilute HBrAq separates as large black octahedra. S.G. $\frac{18}{4}$ = 2·483. Less sol. water than the chloride; 1 pt. dissolves in 530 water at 16°; insol. HBrAq, KBrAq, and alcohol, but sl. sol. in warm water acidulated with HBr, long digestion with this liquid produces roseo-bromide; decomposed to bromopurpureo-chloride by digestion with excess of AgCl; Ag_2O or Ag_2CO_3 produces solutions of roseo-hydroxide and carbonate respectively. Forms double salts, *e.g.* $M.Br_4.6HgBr_2$; $M.(SiF_6)_2$; $M.Br_4.2PtBr_4$ [$M = Co_2(NH_3)_{10}Br_2$].

The following are the chief salts of the *bromopurpureo-* section of purpureo-cobaltic compounds:

$M = Co_2(NH_3)_{10}Br_2$.

Chloride, $M.Cl_4$; double salts, $M.Cl_4.2PtCl_4$, $M.Cl_4.6HgCl_2$ (J.).

Chromate, $M.(CrO_4)_2$ (J.).

Nitrate, $M.(NO_3)_4$ (J.).

Oxalate, $M.(C_2O_4)_2$ (J.).

Sulphate, $M.(SO_4)_2$ (J.).

Dithionate, $M.(S_2O_6)_2$ (J.).

Nitrato-purpureo-cobaltic nitrate $Co_2(NH_3)_{10}(NO_3)_2.(NO_3)_4$ (Genth, *A.* 80, 275; Fremy, *A. Ch.* [3] 35, 257; Gibbs, *Researches*, &c.; also *P. Am. A.* 10, 1; 11, 1). Obtained by dissolving $CoCO_3$ in the minimum of warm dilute HNO_3Aq, adding twice the volume of conc. NH_3Aq, boiling with addition of 127 pts. I for every 59 pts. Co used, filtering after I is all dissolved (from ppd. luteo-salt), and warming the filtrate with HNO_3Aq, whereby I is changed to HIO_3 and the nitrato-salt separates out (Jorgensen, *J. pr.* [2] 23, 227). Red powder with shade of violet; 1 pt. dissolves in 273 pts. water at 16°; decomposed by boiling with water, giving $Co_2O_3.3H_2O$. The nitrato-salts are more easily changed by hot water to roseo-salts than are the chloro- and bromo-purpureo salts. *Basic nitrates* are known; $Co_2(NH_3)_{10}(OH)_2(NO_3)_4.6H_2O$ (Gibbs); and $Co_2(NH_3)_{10}(OH)(NO_3)_5$ (Kunzel, *J. pr.* 72, 209).

The following *nitrato-compounds* form the more important members of the section:

$M = Co_2(NH_3)_{10}(NO_3)_2$.

Chloride, $M.Cl_4$; double salts, $M.Cl_4.2PtCl_4$, $M.Cl_4.2HgCl_2$ (J.).

Bromide, $M.Br_4$ (J.).

Chromate, $M.(CrO_4)_2$.

Dichromate, $M.(Cr_2O_7)_2.2H_2O$ (J.).

Oxalate, $M.(C_2O_4)_2$ (J.).

Sulphate, $M.(SO_4)_2.2H_2O$ (J.).

Dithionate, $M.(S_2O_6)_2.2H_2O$ (J.).

Diamine-cobalt nitrite $M.2[Co_2(NH_3)_4(NO_2)_8]$ (J.).

Sulphato-purpureo-cobaltic sulphate $Co_2(NH_3)_{10}(SO_4).(SO_4)_2.H_2O$ (Gibbs, *P. Am. A.* 10, 1; 11, 1; Jorgensen, *J. pr.* [2] 31, 262). Obtained by adding alcohol to an oxidised ammoniacal solution of $CoSO_4$ (Gibbs), or to a 2½ p.c. aqueous solution of the acid sulphate $Co_2(NH_3)_{10}(SO_4).(SO_4[SO_4H]_2).4H_2O$ (J.). Violet-red, microscopic, dichroic needles; v. sol. water, from which solution roseo-sulphate separates on evaporation. Forms a Pt salt, $Co_2(NH_3)_{10}(SO_4).SO_4.Cl_2.PtCl_4.2H_2O$. The chief *sulphato-salts* are the following:

$M = Co_2(NH_3)_{10}(SO_4)$.

Bromide, $M.(SO_4)Br_2$ (J.).

Nitrate, $M.(SO_4)(NO_3)_2$ (J.)

A few other purpureo-cobaltic salts are known besides those belonging to the four sections already described; the chief are

Purpureo-cobaltic iodide, $Co_2(NH_3)_{10}I_2.I_4$ (J., *J. pr.* [2] 31, 262).

Purpureo-cobaltic chromate and *dichromate*, $Co_2(NH_3)_{10}(OH)_2(CrO_4)_2$, and $Co_2(NH_3)_{10}(Cr_2O_7)_3.H_2O$ (Gibbs).

Division III. *Xantho-cobaltic salts.* These salts are derived from the purpureo-compounds by replacing one-third of the acidic radicle by the group NO_2; they may be called *nitro-purpureo- salts*, $Co_2(NH_3)_{10}R_4.(NO_2)_2$. These salts are produced by the action of nitrous acid or nitrites on ammoniacal solutions of cobaltous salts, or on neutral or acid solutions of purpureo- or roseo-cobaltic salts. The xantho-salts are yellow or brownish yellow; they are more soluble in water, and more easily decomposed by water, than the other salts of the decamine series. By reacting with mineral acids they form purpureo-salts. The following are the chief xantho-salts:—

(Gibbs a. Genth, *Researches on the Ammonia-cobalt bases* [Washington, 1856]).

$M = Co_2(NH_3)_{10}(NO_2)_2$.

Chloride, $M.Cl_4$; double salts, $M.Cl_4.2AuCl_3.2H_2O$; $M.Cl_4.2PtCl_4.2H_2O$; $M.Cl_4.4HgCl_2.2H_2O$.

Iodide, $M.I_4$.

Chromate, $M.(CrO_4)_2.2H_2O$.

Dichromate, $M.(Cr_2O_7)_2$.

Oxalate, $M.(C_2O_4)_2$.

Sulphate, $M.(SO_4)_2$.

Iodo-sulphate, $M.I_2(SO_4)$.

Nitrate, $M.(NO_3)_4$.

Chloro-nitrate, $M.Cl_2(NO_3)_2$; double salts, $M.Cl_2(NO_3)_2.2AuCl_3$; $M.Cl_2(NO_3)_2.PtCl_4$.

Bromo-nitrate, $M.Br_2(NO_3)_2$.

Nitrite, $M.(NO_2)_4.4H_2O$; double salt, $M.(NO_2)_4.2(Co.(NO_2)_3)$.

Series IV. Dodecamines, or Dodecammonio-cobaltic salts, or Luteo-cobaltic salts, $Co_2(NH_3)_{12}R^I_6$. These salts are formed, along with other cobaltamines, by the oxidation of ammoniacal solutions of cobaltous compounds, especially in presence of much salammoniac; they are also produced by treating fusco-cobaltic salts with dilute acids, and by boiling roseo- or purpureo-cobaltic salts with ammonia. The luteo-salts are yellow to bronze-yellow in colour; easily crystallisable; generally more soluble in water than the corresponding roseo-salts. Acid solutions of these salts are stable; aqueous and alkaline solutions are decomposed on boiling with ppn. of $Co_2O_3.3H_2O$. Those luteo-salts which contain water of crystallisation effloresce in air or over H_2SO_4 *in vacuo.* The luteo-salts are closely analogous to the roseo-salts of the decamine series, $Co_2(NH_3)_{10}(OH_2)_2R_6$; the crystalline forms of many luteo- and roseo-salts are the same; the solubilities are similar; both series of salts give similar pps. with $K_4Fe(CN)_6Aq$ and $Na_4P_2O_7Aq$; haloid salts of both series are decomposed by Ag salts giving up the whole of their halogen. Ammonia reacts differently with the two series; the roseo-salts are dissolved with formation of basic compounds, while the luteo-salts are unchanged. Jörgensen (*J. pr.* [2] 31, 49) regards the luteo-salts as roseo-compounds in which $2H_2O$ has been replaced by $2NH_3$.

Luteo-cobaltic chloride $Co_2(NH_3)_{12}Cl_6$ (Mills, *P. M.* [4] 35, 245; Genth, *A.* 80, 275; Braun, *A.* 138, 109; 142, 50; Jörgensen, *J. pr.* [2] 35, 417). Obtained by heating an ammoniacal solution of $CoCl_2$ in presence of NH_4Cl and an oxidiser such as PbO_2, MnO_2, or $KMnO_4$; also by digesting purpureo chloride with NH_3Aq to 50°–60° in a closed tube, and in other ways. Red-yellow, dichroic, monoclinic crystals; S.G. 1·7016 at 20°; when dry it is unchanged in air at 130°; soluble in 16·8 parts water at 11·4° (F. Rose); crystallises from hot water on cooling; aqueous solution is ppd. by alkali chlorides, mineral acids and alcohol; unchanged by heating with conc. HClAq at 100° in a closed tube; slowly decomposed by heating with NH_3Aq, more rapidly by KOHAq. Forms various double salts of which the chief are:—M.2AuCl, (Jorgensen), $M.2PtCl_4.H_2O$, $M.PtCl_4.2H_2O$, $M.3PtCl_4.6H_2O$, $M.3PtCl_4.4H_2O$, $M.2HgCl_2$, $M.6HgCl_2.2H_2O$, $M.3SnCl_2.10H_2O$ (J.; also Braun) [$M = Co_2(NH_3)_{12}Cl_6$].

Luteo-cobaltic sulphate $Co_2(NH_3)_{12}(SO_4)_3.5H_2O$. Obtained by passing air for some days into an ammoniacal solution of $CoSO_4$ and $CoCl_2$ mixed with NH_4Cl, treating the yellow pp. of luteo-chloride and sulphate which forms with hot water, adding Ag_2SO_4 and a few drops of H_2SO_4Aq to the solution, and crystallising by evaporation (Gibbs a. Genth, *Researches*, &c.). Also by rubbing together luteo-chloride and Ag_2O with water, filtering, acidulating the filtrate with H_2SO_4, and evaporating (Jorgensen, *J. pr.* [2] 35, 417). Yellow, rhombic, dichroic, crystals; slightly soluble in cold, more soluble in hot, water; loses $4H_2O$ over H_2SO_4; aqueous solution is only slowly decomposed on boiling; not ppd. by acids from aqueous solution. Forms double salts with sulphates of Ce and La; $M\ 3LaSO_4.H_2O$, $M.3CeSO_4.H_2O$, $M.Ce_2(SO_4)_3.H_2O$ (Wing, *Am. S.* 49, 363). [$M = Co_2(NH_3)_{12}(SO_4)_3$].

The chief *luteo-salts* besides the chloride and sulphate are the following: $M = Co_2(NH_3)_{12}$.

Carbonate, $M.(CO_3)_3.7H_2O$ (Gibbs a. Genth, *Researches*, &c.).

Chromates, $M.(CrO_4)_3.5H_2O$ (G. a. G.).

Dichromate, $M.(Cr_2O_7)_3.xH_2O$.

Bromide, $M.Br_6$; double salt, $M.Br_6.2PtBr_4.2H_2O$ (Jörgensen).

Iodide, $M.I_6$ (J.; G. a. G.).

Nitrate, $M.(NO_3)_6$; double salt, $M.(NO_3)_2.Cl_4.2PtCl_4.2H_2O$ (J.; also Fremy, ***A. Ch.*** [3] 35, 257).

Nitrato-sulphate, $M.(NO_3)_2.(SO_4)_2$ (J.).

Oxalate, $M.(C_2O_4)_3.4H_2O$; double salt, $M.(C_2O_4)_2.Cl_2.2AuCl_3.4H_2O$ (G. a. G.).

Phosphates, $M.(PO_4)_2.8H_2O$ (J.); $M.(PO_4H)_3.4H_2O$ (J.); $M.(P_2O_7Na)_2.23H_2O$ (J.); $M.(P_2O_7)_3.20H_2O$; $M.(P_2O_7H)_2$ (J.).

Chloro-sulphate, $M.(SO_4)_2.Cl_2$; double salts, $M.(SO_4)_2.Cl_2.2AuCl_3$, $M.(SO_4)_2.Cl_2.2HgCl_2$ (J.; G. a. G.; Schiff, *A.* 123, 1; 121, 124; Krok, *Acta Univ. Lund*, 1870).

Bromo-sulphate, $M.(SO_4)_2Br_2$ (J.); double salt, $M.(SO_4)_2.Br_2.2AuCl_3$.

Iodo-sulphate, $M.(SO_4)_2I_2$ (Krok).

Double salts of nitrite, sulphite, and dithionate, $M.(NO_2)_6.Co_2(NO_2)_6$ (Sadtler, *Am. S.* 49, 198); $M.(SO_3)_3.Co_2(SO_3)_3.2H_2O$ (Geuther, *A.* 128, 158; Künzel, *J. pr.* 72, 209); $M.(SO_3)_3.2Co_2(SO_3)_3.15H_2O$ (Geuther, Künzel); $2[M.(S_2O_6)_2.(OH)_2].Co_2(S_2O_6)_2.(OH)_2$ (G.; also K.).

COBALTAMINES NOT INCLUDED IN ANY OF THE FOREGOING CLASSES.

Erdmann's salt $Co_2(NH_3)_4(NO_2)_8K_2$ (Erdmann, *J. pr.* 97, 405). Brown, lustrous, prisms, separating from a solution of $CoCl_2$ in presence of much NH_4Cl on addition of KNO_2. Solutions of this salt give pps. of analogous compositions with solutions of many metallic salts, *e.g.* of Pb, Hg, Ag, Tl (Gibbs, *P. Am. A.* 10, 1; 11, 1).

Melano-cobaltic chloride $Co_2(NH_3)_6.NH_2Cl.Cl_4$ (F. Rose; Vortmann, *B.* 10, 1451; 15, 1890). Greyish violet, very hygroscopic, crystals; obtained by oxidising an ammoniacal solution of a cobaltous salt, adding HClAq, filtering after an hour or so from purpureo-chloride, and dropping the filtrate into an equal volume of ice-cold fuming HClAq. This compound forms double salts, and derivatives, especially $M.Cl_4.PtCl_4$, $M.(OH)_2.Cl_2.PtCl_4$, $M.(OH)_2.Cl_2.3HgCl_2.H_2O$ (Vortmann). [$M = Co_2(NH_3)_6.NH_2Cl$.].

Ammonio-cobaltic oxychloride $Co_3(NH_3)_2O_3Cl_2.5H_2O$ (Fremy, *A. Ch.* [3] 35, 257). Black crystals; obtained by exposing ammoniacal $CoCl_2Aq$ to the air for some months, boiling with NH_3Aq, filtering from purpureo-chloride, and boiling again. M. M. P. M.

COBALTATES. When CoO, $Co(OH)_2$, or $CoCO_3$ is dropped into 6–8 parts molten potash, a blue colour is formed which after a time changes to brown; if fusion is continued until dark-coloured crystals begin to form, the mass is then allowed to cool and treated with water, thin, black, lustrous, six-sided tablets remain. These crystals have the composition $(Co_3O_5)_3.K_2O.xH_2O$; according to Schwarzenberg $x = 3$, or if the crystals are dried at 200° $x = 1$ (*A.* 97, 212; also Mayer, *A.* 101, 266). Von Pebal (*A.* 100, 257) says that all water is removed at 100°. The crystals of *potassium cobaltate* are insoluble in water; they are decomposed at a little over 200°, water then dissolves out K_2O and Co_3O_4 remains. Mayer (*l.c.*) says that long-continued washing or boiling with water removes potash from the original crystals, and that dilute HClAq removes Co (*cf.* also Russell, *Pr.* 32, 258). M. M. P. M.

COBALTI-CYANIDES and **COBALTO-CYANIDES** *v.* CYANIDES.

COBALT COLOURING MATTERS. Addition of a Co salt to potash glass produces a deep blue colour. Roasted Co ore is fused with pearl-ash and quartz-sand, the molten mass is poured into water, and then finely powdered; it is used as a colouring matter under the name of *Smalt*. Smalt is essentially a double silicate of Co and K approaching the composition $CoO.K_2O(SiO_2)_6$. *Cobalt-ultramarine* or *Thénard's blue*, and *Cœruleum*, are essentially salts of Co chiefly phosphates and arsenates. *Cobalt-green* or *Rinman's green* contains Co and Zn oxides, and sometimes a little As_2O_3; it is prepared by evaporating mixed solutions of Co and Zn salts and strongly heating the residue. (For details of these colouring matters *v.* DICTIONARY OF TECHNICAL CHEMISTRY.) M. M. P. M.

COBRA POISON (A. Pedler, *Pr.* 27, 17; Blyth, *Analyst*, i. 204; Warden, *C. N.* 54, 197). Two-thirds of the organic matter in the poison of *Naja tripudians* is of albuminous character, being ppd. by alcohol, the poisonous substance is soluble in alcohol. NH_3 is not an antidote, but HCl retards the physiological action, while HCl and platinic chloride form a salt, $(C_{17}H_{25}N_4O_7,HCl)_2PtCl_4$(?), which is not poisonous. $AuCl_3$ and $KMnO_4$ mixed with the poison before injection prevent death; but after the poison has been injected, the subsequent injection of these liquids will not prevent death (T. L. Brunton a. Sir J. Fayrer, *Pr.* 27, 465). A poisonous crystalline substance may be obtained by dialysing the poison.

COCAÏNE $C_{17}H_{21}NO_4$. *Benzoyl-methyl-ecgonine.* [98°]. S. ·14 at 12°.

Occurrence.—In the leaves of *Erythroxylon Coca* of South America (Niemann, *Ar. Ph.* [2] 103, 120, 291; *A.* 114, 213). These leaves are chewed by the inhabitants.

Formation. In small quantity by heating together ecgonine, benzoic anhydride and methyl-iodide at 100° for 10 hours (Merck, *B.* 18, 2952).

Preparations.—1. Coca leaves are digested with ether; the ether is evaporated and the residue extracted with boiling water; the solution is mixed with magnesia and evaporated and the cocaine extracted by amyl alcohol (Trupheme, *C. C.* 1881, 417).—2. The leaves are extracted with alcohol, colouring matter is ppd. by lime, and the filtrate evaporated to a small bulk and mixed with water. The alkaloid is then ppd. by K_2CO_3 and dissolved in ether and decolorised by animal charcoal (Schull, *Ph.* [3] 10, 408).

Properties. Small monoclinic prisms; *a*:*b*:*c* = 1·186:1:1·223; $\beta = 73°\ 50'$ (Tschermak, *Sitz. W.* 48, i. 34); v. sl. sol. water, v. sol. hot alcohol and ether. Conc. H_2SO_4 dissolves it without colour. It produces insensibility to pain in the tongue, eye, or other part touched by it. Taken internally it acts somewhat like opium (Kennedy, *Ph.* [3] 10, 65; J. Grasset, *C. R.* 99, 983, 1122; 100, 364; Richard, *C. R.* 100, 1409; Laffont, *C. R.* 105, 1278; Sighicelli, *C. C.* 1887, 1150). An injection of cocaine acts as a cerebro-spinal stimulant or anti-narcotic (Mosso, *Ar. Ph.* [3] 26, 179). Solutions of salts of cocaine are ppd. by KOH, NH_3, and Na_2CO_3; the pp. is soluble only in a large excess of KOH, but insol. NH_3. Ammonium carbonate gives a pp. sol. excess. Picric acid, tannin and HCl, potassio-mercuric iodide, iodine solution, $SnCl_2$, $AuCl_3$, and $PtCl_4$ also give pps. By heating with conc. HCl cocaine is split up into ecgonine $C_9H_{15}NO_3$, methyl alcohol, and benzoic acid (Lossen, *A.* 133, 351). Cocaine, freshly ppd. by NH_3 and left under water, slowly decomposes forming MeOH and benzoyl-ecgonine (Paul, *Ph.* [3] 18, 783). The specific rotation in chloroform solution at 20° is given by the formula: $[\alpha]_D = -(15{\cdot}827 + {\cdot}00585\,q)$, where q = weight of chloroform in 100 pts. by weight of the solution, and the tube is 100 mm. long. If $q = 0$ then $[\alpha]_D = -15{\cdot}827$.

Salts.—B′HCl: the melting-point varies in different preparations between [181°] and [185°]. For its medicinal employment its absolute purity is essential, and this is best determined by taking its specific rotation. In dilute alcoholic solution at 20°, with a tube 100 mm. long, the specific rotation is given by the formula: $[\alpha]_D = -(52{\cdot}18 + {\cdot}1588\,q)$, and $[\alpha]_D = -(67\ 982 - {\cdot}15827\,c)$, where q = weight of dilute alcohol of S.G. $\frac{20}{4}$ ·9353 (mixture of 6 pts. by weight of absol. alcohol to 9 pts. by weight of water) in 100 pts by weight of the solution, and c = weight of cocaine hydrochloride in 100 pts. by vol. of the solution. When $q = 0$, then $[\alpha]_D = 52{\cdot}2$; when $q = 100$, then $[\alpha]_D = 68{\cdot}0$ (Antrick, *B.* 20, 310).—$B'_2H_2PtCl_6$.—$B'HAuCl_4$.—$B'H_2C_2O_4$: feathery crystals.

Amorphous cocaine. An amorphous alkaloid accompanies cocaine in coca-leaves. It is v. sol. alcohol and ether. Its hydrochloride is amorphous, and its solution partially decomposes on evaporation, becoming acid (Paul, *Ph.* [3] 18, 784). According to Hesse (*Ph.* [3] 18, 71) this base is isomeric with cocaine (*cf.* Stockman, *Ph.* [3] 17, 861; Howard, *Ph.* [3] 18, 71; Bender, *C. C.* 1885, 490. *V. also* ECGONINE).

COCATANNIC ACID $C_{14}H_{18}O_4$. [189°]. Occurs in coca leaves (Warden, *Ph.* [3] 18, 985). Gives a red colour with KOH. $FeSO_4$ and Fe_2Cl_6 give a dark-green colour. $Pb(OAc)_2$ gives a rose-red pp. It reduces alkaline silver solution, but not Fehling's solution. Potash-fusion gives butyric and traces of benzoic acids.

COCCERIC ACID $C_{31}H_{62}O_3$. [93°]. Formed, together with cocceryl alcohol, by saponification of coccerin, the wax of cochineal. White crystalline powder. Sol. hot alcohol, ether, benzene, &c., sl. sol. the cold solvents. On oxidation with CrO_3 and acetic acid it gives pentadecoic acid, the same product as from cocceryl alcohol (Liebermann a. Bergami, *B.* 20, 961).—A'_2Ca and A'_2Ba: flocculent pps.

Ethyl ether A′Et [c. 70°] (Liebermann, *B.* 18, 1980).

COCCERIN $C_{30}H_{60}(O.C_{31}H_{61}O_2)_2$. *Cocceryl coccerate.* [106°]. Occurs in cochineal in quantity varying from 1 p.c. to 4 p.c. and is obtained by extraction with benzene. The cocoons of the cochineal insect consist of coccerin to the extent of ¾ of their weight (Liebermann, *B.* 19, 328). Thin glistening plates. Sl. sol. all cold solvents, nearly insol. alcohol and ether. On saponification with alcoholic KOH it gives cocceryl alcohol $C_{30}H_{60}(OH)_2$ and cocceric acid $C_{31}H_{62}O_3$ (Liebermann, *B.* 18, 1975).

COCCERYL ALCOHOL $C_{30}H_{60}(OH)_2$. [101°–104°]. Formed, together with cocceric acid, by saponification of coccerin, the wax of cochineal (Liebermann, *B.* 18, 1975). White crystalline powder. On oxidation with CrO_3 and acetic acid it gives pentadecoic acid $C_{15}H_{30}O_2$ and probably also an acid $C_{30}H_{60}O_3$.

Acetyl derivative $C_{30}H_{60}(OAc)_2$: [50°]; crystalline solid; v. sol. ether, warm alcohol, and acetic acid; v. sl. sol. acetone.

Benzoyl derivative $C_{30}H_{60}(OBz)_2$: [62°]; crystalline solid; v. sol. ether, warm alcohol, and acetic acid, v. sl. sol. acetone (Liebermann a. Bergami, *B.* 20, 959).

COCCININ *v.* CARMINIC ACID.

COCCOGNIN $C_{20}H_{22}O_8$. A crystalline substance occurring in the seeds of *Daphne Mezereum.* Sl. sol. water, v. sol. alcohol and ether. May be sublimed, when it emits an odour like coumarin. Boiling dilute H_2SO_4 forms no glucose from it (Casselmann, *Z.* [2] 6, 681).

COCCULIN $C_{19}H_{26}O_{10}$. Occurs in cocculus indicus. Found in small quantities in the preparation of picrotoxin (*q. v.*), from which it can be separated by means of absolute alcohol, and recrystallised from hot water acidulated with HCl. Conc. H_2SO_4 colours it pale yellow, disappearing on stirring (Löwenhardt, *A.* 222, 353).

COCETHYLINE $C_{18}H_{23}NO_4$. [109°]. Obtained by heating benzoyl-ecgonine with ethyl iodide for 8 hours at 100°. Splendid glistening prisms. Has an anæsthetic action. $PtCl_4$ gives with very dilute solutions of the hydrochloride a yellow pp. of the platino-chloride $B'_{12}H_2Cl_2PtCl_4$, which crystallises from a large quantity of hot water in glittering yellow rhombic plates. $AuCl_3$ gives a very sparingly soluble yellow pp. $HgCl_2$ forms a white pp., v. sol. hot water (Merck, *B.* 18, 2954).

COCHLEARIA OIL. The essential oil of scurvy-grass (*Cochlearia officinalis*) is isobutyl thiocarbimide (Hofmann, *B.* 7, 508).

COCOA NUT OIL *or cocoa butter.* The following acids have been described as present in the product of saponification of this fatty oil: hexoic, octoic, decoic, lauric $C_{12}H_{24}O_2$, an isomeride of lauric [58°], tridecoic $C_{13}H_{26}O_2$, myristic, palmitic, stearic, oleic, and arachic acids. Kingzett (*C. J.* 33, 38) also found an acid $C_{61}H_{128}O_2$ [72°] (Bromeis, *A.* 35, 86; Fehling, *A.* 53, 399; Gœrgey, *A.* 66, 290; Oudemans, *J. pr.* 81, 367; Carr Robinson, *Tr. E.* 28, 277; Traub, *Ar. Ph.* [3] 21, 19).

CODAMINE $C_{20}H_{25}NO_4$. [126°] (from benzene); [121°] (from alcohol or ether). An alkaloid occurring in the aqueous extract of opium (Hesse, *A.* 153, 56; *Suppl.* 8, 280). Six-sided prisms (from ether); m. sol. boiling water, v. sol. benzene, alcohol, chloroform, and ether. Conc. HNO_3 gives a green solution. Fe_2Cl_6Aq gives a green colour. Conc. H_2SO_4 gives a blue colour, changing to green, and to dark violet on warming. NH_3 and KOH give pps. sol. excess.—$B'_2H_2PtCl_6$ 2aq. B'HI $1\frac{1}{2}$aq.

CODEÏNE $C_{18}H_{21}NO_3$. *Methyl-morphine. Codeia.* [150°]. S.G. 1·32. S. 1·26 at 15°, 5·88 at 100°. $[\alpha]_D = -134°$ (in alcohol). S. (amyl alcohol) 15·68; S. (benzene) 9·60 (Kubly, *J.* 1866, 823).

Synthesis.—By gently heating morphine (1 mol.) with NaOH (1 mol.) and MeI (1 mol.) dissolved in alcohol (Grimaux, *C. R.* 92, 1140, 1228; Hesse, *A.* 222, 210). The yield is small, but by doubling the quantity of MeI a good yield of codeïne methylo-iodide may be obtained. The codeïne so prepared is lævorotatory; $[\alpha]_D = -130°$.

Preparation.—Aqueous extract of opium is freed from meconic acid by ppg. with $CaCl_2$, and the filtrate evaporated to crystallisation. The mixed hydrochlorides of morphine and codeïne are dissolved in water and ppd. by ammonia; morphine is ppd. but codeine remains in solution. On evaporating the filtrate codeine hydrochloride crystallises out (Robiquet, *A. Ch.* [2] 51, 259; *A.* 5, 106; Gregory, *A.* 7, 263; Anderson, *A.* 77, 341; *Ed. Phil. Trans.* 20, 57; *cf.* Couerbe, *A. Ch.* [2] 59, 158; Regnault, *A. Ch.* [2] 68, 136; Gerhardt, *Rev. Scient.* 10, 203; Winckler, *Rép. Pharm.* 44, 459; Merck, *A.* 11, 279; Plugge, *Ar. Ph.* [3] 25, 343).

Properties.—Trimetric crystals (containing aq). From CS_2 it separates in anhydrous trimetric crystals $a:b:c = \cdot930:1:\cdot509$ (Arzruni, *Z. K.* 1, 302). Lævorotatory; $[\alpha]_j$ (in alcohol) $= -136°$; (in $CHCl_3$) $= -112°$ (Hesse, *A.* 176, 191; *cf.* Grimbert, *J. Ph.* [5] 16, 295). The rotatory power is much affected by the presence and amount of acid in solution (Hesse; Tykocimer, *R. T. C.* 1, 144). It is a strong base, reddens litmus, and pps. salts of Pb, Fe, Cu, &c. Sol. ether. Codeine is insoluble in aqueous KOH and hardly more soluble in aqueous NH_3 than in pure water. Its physiological action resembles that of morphine.

Colour reactions.—1. H_2SO_4 forms a greenish solution which, after a week, becomes indigo blue.—2. Fe_2Cl_6 gives no colour.—3. H_2SO_4 and Fe_2Cl_6 gives an intense blue (Lindo, *C. N.* 37, 158).—4. Chloride of iodine gives a yellowish pp. in solutions of salts of codeine.—5. K_2CrO_4 gives the chromate. 6. K_4FeCy_6 gives no pp. (Plugge, *Ar. Ph.* [3] 25, 793).

Reactions.—1. Hot H_2SO_4 decomposes it, and after diluting, Na_2CO_3 pps. 'amorphous codeine' as a grey powder [100°], v. sol. alcohol, but ppd. therefrom by ether.—2. Heating with KOH gives off trimethylamine.—3. Heating with a large excess of conc. HClAq forms 'chlorocodide' $C_{18}H_{20}ClNO_2$, apomorphine, and MeCl.—4. HBr gives 'bromocodide' $C_{18}H_{20}BrNO_2$, 'deoxy-codeine' $C_{18}H_{21}NO_2$ (sol. ether), and 'bromo-tetracodeine' $C_{72}H_{83}BrN_4O_{12}$ (insol. ether) (Matthiessen a. Wright, *Pr.* 17, 460; 18, 83; Wright, *Pr.* 19, 371, 504).—5. HI and P at 100° to 130° forms some amorphous substances (Wright, *Pr.* 20, 8).—6. Codeine (1 pt.) evaporated with HPO_3 (3 pts.) and water (5 pts.) is partly converted into dicodeine $C_{36}H_{42}N_2O_6$ and tetracodeine $C_{72}H_{84}N_4O_{12}$ (Matthiessen a. Wright, *Pr.* 18, 87).—7. Alkaline $KMnO_4$ expels half the nitrogen as NH_3 (Wanklyn a. Gamgee, *C. J.* 21, 25).—8. PCl_5 forms two bases $C_{18}H_{20}ClNO_2$ and $C_{18}H_{19}Cl_2NO_2$ (v. Gerichten, *A.* 210, 107).—9. *Cyanogen*, passed into a conc. alcoholic solution of codeine, forms crystals of $C_{18}H_{21}NO_3Cy_2$.

Salts.—B'HCl 2aq; radiate groups of prisms. S. 5 at 15·5° $[\alpha]_j = -108°$.—$B'_2H_2PtCl_6$ 4aq: light yellow powder, gradually becoming crystalline.—B'HI aq: long thin needles. S. 1·3.—$B'HI_3$: red crystals with violet reflex.—$B'HI_5$.—$B'HNO_3$: small prisms, v. sol. hot water.—$B'_2H_2C_2O_4$ 3aq: prisms or scales. S. 3·3 at 15·5°; 200 at 100°.—$B'H_3PO_4$ $1\frac{1}{2}$aq: scales or prisms.—$B'_2H_2SO_4$ 5aq: trimetric prisms. S. 3·3 in the cold $[\alpha]_j = -101°$ at 20°.—$B'H_2S_2O_3$ 5aq: prisms. S. 5·5.—B'HSCy $\frac{1}{2}$aq. [100°]. Radiating needles. **Chloro-acetate** $B'C_2ClH_3O_2$ [154°].—**Di-chloro-acetate** $B'C_2Cl_2H_2O_2$ [156°].—**Tri-chloro-acetate** $B'C_2Cl_3HO_2$. [93°].—**Chloro-crotonate** $B'C_4H_5ClO_2$. [171°].—**Tri-chloro-butyrate** $B'C_4H_5Cl_3O_2$ [173°].—**Di-bromo-pyruvate** $B'C_3H_2Br_2O_3$ [70°] (Daccomo, *J.* 1884, 1385).

Acetyl derivative $C_{18}H_{20}AcNO_3$. [135°]. From codeine and Ac_2O (Wright, *C. J.* 27, 1031; Hesse, *A.* 222, 212).—B'HCl 2aq.—$B'_2H_2PtCl_6$.

Propionyl derivative $C_{18}H_{20}(C_3H_5O)NO_3$. From codeïne and propionic anhydride. V. sol. alcohol, ether, and benzene. Conc. H_2SO_4 gives a blue colour. Forms well-crystallised salts.—B'HCl 2aq.—$B'_2H_2PtCl_6$.—B'HI aq.—$B'H_2C_2O_4$ 8aq (Hesse, *A.* 222, 212).

Butyryl derivative $C_{18}H_{20}(C_4H_7O)NO_3$.

Amorphous (Beckett a. Wright, *C. J.* 28, 15).—$B'HCl\ 3aq$.—$B'_2H_2PtCl_6$.

Benzoyl derivative $C_{18}H_{20}(C_7H_5O)NO_3$. Crystallises from ether.—$B'HCl\ aq$.—$B'_2H_2PtCl_6$.

Succinoxyl derivative $C_{18}H_{20}NO_3(CO.CH_2.CH_2.CO_2H)\ 5aq$. Formed by heating codeine (1 pt.) with succinic acid (2 pts.) at 180° (Beckett a. Wright, *C. J.* 28, 689). Insol. water, ether, and benzene.—$B'HCl\ aq$.—$B'_2H_2PtCl_6$.

Camphoryl derivative $C_{18}H_{20}NO_3(C_{10}H_{15}O_3)$. From codeine and camphoric acid at 180°. Crystalline.—$B'HCl\ 3aq$.—$B'_2H_2PtCl_6$.

Methylo-iodide $C_{18}H_{21}NO_3MeI$. Prepared from codeine and methyl iodide, or from morphine, methyl iodide and sodium in presence of alcohol. Fine needles when hydrated: hard voluminous crystals when anhydrous. With moist silver oxide yields a hydroxyl derivative converted by dehydration into methyl codeine (*q. v.*) (Grimaux, *A. Ch.* [5] 27, 276; *C. R.* 93, 591). By successive treatment with Ac_2O and AgOAc it is converted into $C_{17}H_{14}O_3$ [131°] which crystallises from alcohol in needles (Fischer, *B.* 19, 794).

Ethylo-iodide $C_{18}H_{21}NO_3EtI$. Formed by heating codeine with EtI and alcohol at 100° (How, *C. J.* 6, 125). Crystalline mass, v. sol. water. Not decomposed by KOH but converted by Ag_2O into a very alkaline hydroxide. The hydroxide changes, when its alkaline solution is evaporated, into ethyl-codeine. Acetyl derivative $C_{18}H_{20}AcNO_3EtI\ \frac{1}{2}aq$: crystals, v. sl. sol. cold alcohol (Beckett a. Wright, *C. J.* 28, 318). Gives rise to $C_{18}H_{20}AcNO_3EtCl$ and $(C_{18}H_{20}AcNO_3EtCl)_2PtCl_4$. Butyryl derivative $C_{18}H_{20}(C_4H_7O)NO_3EtI\ \frac{1}{2}aq$.

Chloride $C_{18}H_{20}ClNO_2$. *Codeyl chloride.* [147°]. Formed by treating codeine with PCl_5 mixed with $POCl_3$. Colourless leaflets; insol. water, sol. alcohol and ether (v. Gerichten, *A.* 210, 105).—$B'_2H_2PtCl_6$.

Chloro-codide $C_{18}H_{20}ClNO_2$. Formed by prolonged heating of codeine (1 pt.) with conc. HCl (12 pts.) at 100° (Matthiessen a. Wright, *Pr.* 17, 460; 18, 83; *A. Suppl.* 7, 364). Amorphous; v. sol. alcohol and ether. Water at 140° gives HCl and codeine. Conc. HCl at 140° gives MeCl and apomorphine.—$B'HCl$: amorphous.—$B'_2H_2PtCl_6$.

Bromo-codide $C_{18}H_{20}BrNO_2$. From codeine and HBrAq (S.G. 1·5) at 100° (Wright, *Pr.* 19, 371). Unstable.—$B'HBr$: gummy.

Chloro-codeine $C_{18}H_{20}ClNO_3\ 1\frac{1}{2}aq$. [170°]. From codeine, $KClO_3$, and HCl. Crystalline powder: sl. sol. ether and hot water, v. e. sol. NH_3Aq. $B'_2H_2SO_4\ 4aq$: prisms.—$B'_2H_2PtCl_6$.

Chloride $C_{18}H_{19}Cl_2NO_2$. *Chloro-codeyl chloride.* [196°]. Formed by heating codeine (1 mol.) with PCl_5 ($2\frac{1}{2}$ mols.) and $POCl_3$ at 70° (v. Gerichten, *A.* 210, 105). Trimetric prisms; insol. water, v. sol. alcohol, ether, and benzene. Its hydrochloride crystallises in grouped needles.—$B'_2H_2PtCl_6$.

Bromo-codeïne $C_{18}H_{20}BrNO_3$. [162°]. From codeine and bromine-water. Needles (containing $\frac{1}{2}$ aq or $1\frac{1}{2}$ aq). V. sl. sol. water, v. e. sol. NH_3Aq.—$B'_2H_2PtCl_6$.—$B'HBr\ aq$: prisms.

Ethylo-hydrate B'EtOH. Decomposes on evaporation of its aqueous solution forming bromo-ethyl-codeine (*B.* 15, 1485).

Chloride $C_{18}H_{19}BrClNO_2$. [131°]. From bromo-codeine and PCl_5. Prisms; sol. alcohol and ether.

Tri-bromo-codeine $C_{18}H_{18}Br_3NO_2$. From bromo-codeine and bromine-water (Anderson). Amorphous powder.—B'_23HBr.—$B'_2H_2PtCl_6$.

Di-iodo-codeine $C_{18}H_{19}I_2NO_3$ (?). From codeine hydrochloride and ICl. Crystals (from alcohol). Insol. water.—$B'_2H_2PtCl_6\ aq$.

Nitro-codeine $C_{18}H_{20}(NO_2)NO_3$. From codeïne and hot dilute HNO_3 (S.G. 1·06). Silky laminæ (from alcohol). Sl. sol. boiling water (Anderson).—$B'_2H_2PtCl_6\ 4aq$.—$B'_2H_2SO_4\ 2aq$ (at 100°): radiating needles.

Dicodeine $(C_{18}H_{21}NO_3)_2\ 2aq$. Formed by heating codeine with dilute H_2SO_4, with P_2O_5, or with oxalic acid (Anderson, *Ed. Phil. Trans.* 20 [1] 57; Armstrong, *C. J.* 24, 56; Wright, *C. J.* 25, 506; 28, 312, 696). Amorphous powder. Insol. water, sol. alcohol and ether. Immediately ppd. from its salts by Na_2CO_3 (codeine comes down only after some time). Fe_2Cl_6 gives no colour. HNO_3 gives a pale orange tint. Hot conc. HCl converts it into $C_{72}H_{83}ClN_4O_{11}H_4Cl_4$. HI and phosphorus at 120° form $C_{136}H_{153}IN_8O_{20}H_8I_8$ (?).

Salt.—$B''H_2Cl_2\ 6aq$.

Acetyl derivative $(C_{18}H_{20}AcNO_3)_2$. From dicodeine and Ac_2O (Beckett a. Wright, *C. J.* 28, 15). Amorphous; v. sol. ether. $B''H_2Cl_2\ 5aq$: crystalline.—$B''H_2PtCl_6$.

Tricodeine $(C_{18}H_{21}NO_3)_3$. A product of the action of H_2SO_4 or of $ZnCl_2$ on codeine (Wright, *C. J.* 25, 507; 27, 101; *Pr.* 20, 203). Amorphous. Sol. alcohol and ether. Its hydrochloride is amorphous and extremely deliquescent. Conc. HCl converts it on heating into apocodeine. Fe_2Cl_6 gives no colour at first, but afterwards a reddish-purple. HNO_3 gives a blood-red colour. Na_2CO_3 immediately pps. it from solutions of its salts (difference from codeine). Hot concentrated hydrochloric acid forms $C_{108}H_{111}N_6O_{12}H_6Cl_6$.

Tetracodeine $(C_{18}H_{21}NO_3)_4$. From codeine and P_2O_5. Formed also by boiling codeine with benzene and NaOEt (Wright, *C. J.* 27, 107; 28, 324). Amorphous; sol. alcohol; insol. ether. Its hydrochloride is amorphous and deliquescent. Fe_2Cl_6 gives immediately a reddish-purple colour. HNO_3 gives a blood-red colour. $K_2Cr_2O_7$ and H_2SO_4 gives an evanescent red colour (this reaction is given also by tricodeine, but no colour is got with codeïne or dicodeine). Na_2CO_3 immediately pps. tetracodeine from its salts. Boiling aqueous HCl has no action. Boiling HI and phosphorus form $C_{136}H_{150}I_2N_8O_{22}H_8I_8$ (?).

Acetyl derivative $(C_{18}H_{20}AcNO_3)_4$. From tetracodeine and Ac_2O at 120°. Amorphous.—$B''_2H_2PtCl_6$.

Bromo-tetracodeïne $C_{72}H_{83}BrN_4O_{12}$. From codeine and HBr. HCl forms $C_{72}H_{83}ClN_4O_{12}H_4Cl_4$. Hydric bromide forms bromo-tetramorphine $C_{68}H_{75}BrN_4O_{12}$.

Salt. $C_{72}H_{83}BrN_4O_{12}H_4Br_4$.

Deoxycodeine $C_{18}H_{21}NO_2$. From codeine and HBr. Insol. water, sol. alcohol and ether. Turns brown in air.—$B'HBr$: small crystals.

Apocodeine $C_{18}H_{19}NO_2$. Formed by heating codeine hydrochloride with a conc. solution of $ZnCl_2$ for 15 minutes (Matthiessen a. Burnside, *Pr.* 19, 71). Gummy mass; insol. water, sol. alcohol and ether. Gives a blood-red colour with HNO_3.—B′HCl: amorphous. Acts as a mild emetic.

Methyl-codeïne $C_{19}H_{23}NO_3$. *Di-methyl-morphine.* [119°]. Prepared by evaporating the product of the action of silver oxide, or of KOH, on codeine methylo-iodide. The substance separates out as an oil, which solidifies on desiccation. Hard, brilliant laminæ. It appears to possess all the properties of a tertiary base and to be formed by the dehydration of methyl codeine hydroxide. With sulphuric acid it gives a brown colouration, turning violet on addition of water (Grimaux, *A. Ch.* [5] 27, 283).

Ethyl-codeïne $C_{18}H_{20}EtNO_3$. Formed by evaporation of a solution of codeine ethylo-hydroxide.

Methylo-iodide $C_{18}H_{20}EtNO_3MeI$. Readily formed by the union of MeI with ethyl-codeine.

Methylo-hydroxide B′MeOH. Formed by the action of moist Ag_2O on the methylo-iodide. On heating to 130° it decomposes into methyl-ethyl-propyl-amine and a body $C_{15}H_{10}O_2$ (Gerichten a. Schrötter, *B.* 15, 1486). The compound $C_{15}H_{10}O_2$ [65°] is converted into phenanthrene by distillation with zinc-dust. According to Grimaux (*C. R.* 93, 591), a crystalline tertiary base (? methyl-ethyl-codeine) [132°] is formed by heating ethyl-codeine methylo-iodide with moist Ag_2O or KOH.

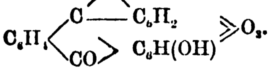
Bromo-ethyl-codeïne $C_{18}H_{19}EtBrNO_3$. Long white needles. Sol. acids and strong NH_3. Tertiary base. Formed by evaporation of a solution of the ethylo-hydrate of bromo-codeine.

Ethylo-hydrate B′MeOH. Formed by the action of moist Ag_2O on the methylo-iodide. On evaporating the solution to dryness it decomposes into methyl-ethyl-propyl-amine and a body $C_{15}H_9BrO_2$ (Gerichten a. Schrötter, *B.* 15, 1485). This compound $C_{15}H_9BrO_2$ [122°] is converted by CrO_3 into a substance which is apparently a quinone.

DICODETHINE *v. Ethylene*-MORPHINE.

CODETHYLENE *v. Ethyl*-MORPHINE.

CŒRULEÏN $C_{20}H_8O_6$ *i.e.*

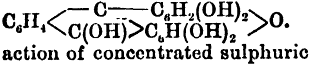


Formation.—1. By heating galleïn with concentrated sulphuric acid at 190°–200°, an olive-brown solution is formed, from which the cœruleïn is precipitated by water.—2. By oxidation of cœrulin.

Properties.—Dark-blue, metallic glistening crystals, sl. sol. water, alcohol and ether. When heated with *zinc-dust* phenyl-anthracene is produced.

Triacetyl derivative $C_{20}H_7O_3(OAc)_3$, red needles, sol. alcohol, acetone and chloroform, readily decomposed with separation of cœrulein (Buchka, *A.* 209, 272).

CŒRULIN $C_{20}H_{12}O_7$ *i.e.*



$C_6H_4\left\langle\begin{matrix}—C——C_6H_2(OH)_2\\ C(OH)>C_6H(OH)_2\end{matrix}\right\rangle O$. Formed by the action of concentrated sulphuric acid on gallin; formed also by reduction of cœruleïn with ammonia and zinc-dust (Baeyer, *B.* 4, 556, 663): the solution is acidified and agitated with ether, on evaporation of which cœrulin is left as a red substance, sol. alcohol, ether and acetic acid with golden-green fluorescence. It is readily oxidised to cœruleïn.

Tetra-acetyl derivative $C_{20}H_8O_2(OAc)_4$. [256°]. Cannot be prepared directly from cœrulin, but indirectly from cœruleïn, acetic anhydride and zinc-dust; yellow needles sol. alcohol, chloroform and benzene, converted on oxidation into tri-acetyl-cœrulein.

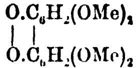
Constitution.—Cœrulin bears to gallin (*q. v.*) the same relation that phenol-phthalidin bears to phenol-phthalin, as shown by its analogous method of formation (Buchka, *A.* 209, 274).

CŒRULIGNOL $C_{10}H_{14}O_2$ *i.e.* $C_9H_{10}(OMe)(OH)$. *Blue-oil.* (241° cor.). S.G. ^{15} 1·06. Obtained first by Reichenbach among the higher boiling portions of beech-tar oil, and characterised by giving a blue colouration with baryta water. Is best separated by boiling the oil for some time with acetic acid just strong enough to dissolve it. On pouring the solution into water the compound separates out. Colourless oil, of creasote-like odour, m. sol. hot water, alcohol, ether and acetic acid. From its reaction with nitrobenzene and strong sulphuric acid it appears to be a homologue of pyrocatechin, probably of guaiacol (Pastrovich, *M.* 4, 188). It gives a blue colouration with *baryta water* or *bleaching powder*; with *ferric chloride* in alcoholic solution, a green, but in aqueous solution, a carmine-red colouration. Heated with *hydrochloric* acid it forms a substance $C_9H_{12}O_2$ *i.e.* $C_9H_{10}(OH)_2$ crystallising in prisms [56°]. On melting it evolves methyl chloride.

Acetyl derivative $C_{10}H_{13}AcO_2$ (265°); viscid, colourless oil, once obtained in fan-shaped crystals.

Nitro-derivative $C_{10}H_{13}NO_2O_2$ [124°], obtained together with oxalic acid, the principal product, by the action of nitric acid (S.G. 1·12) on cœrulignol. Light yellow crystals, sol. water and alcohol.

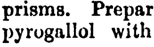
CŒRULIGNONE $C_{16}H_{16}O_6$ *i.e.*



$\begin{matrix}O.C_6H_2(OMe)_2\\ |\;\;|\\ O.C_6H_2(OMe)_2\end{matrix}$

Tetramethyl-ether of *tetra-oxy-diphenylene-quinone. Cedriret.* One of the products obtained by Reichenbach from beechwood tar (*J. pr.* 1, 1). The crude acetic acid prepared from wood is treated with $K_2Cr_2O_7$ which oxidises the di-methyl-ether of pyrogallol that is present (Liebermann, *B.* 5, 746; 6, 381; *A.* 169, 231; Hofmann, *B.* 11, 335). It is purified by solution in phenol and ppn. by alcohol or ether. Small dark steel-blue needles. Insol. ordinary solvents; cannot be distilled. Dissolves in conc. H_2SO_4 with blue colour, but is decomposed thereby with elimination of one or two methyl groups. Heated with aqueous KOH it forms a green solution, quickly becoming yellow. *Potash-fusion* gives an intense but fugitive violet colour. Reducing agents convert it into hydrocœrulignone $C_{16}H_{18}O_6$ [190°] which is the tetra-methyl-ether of HEXA-OXY-DIPHENYL (*q. v.*).

Cœrulignone of the ethyl series



$\begin{matrix}C_6H_2(OEt)_2.O\\ |\qquad\qquad|\\ C_6H_2(OEt)_2.O\end{matrix}$

Greenish-golden glistening prisms. Prepared by the oxidation of diethyl-pyrogallol with chromic acid in acetic acid.

May be reduced to the hydro-derivative $C_6H_2(OEt)_2(OH).C_6H_2(OEt)_2(OH)$ [176°] which crystallises in long white needles (Hofmann, *B.* 11, 801).

Di-bromo-hydrocœrulignone *v.* Hexa-oxy-diphenyl.

COFFEE *v.* Caffeine and Caffeol.

COLCHICINE $C_{22}H_{25}NO_6$ *i.e.* $C_{15}H_9(OMe)_3(NHAc)(CO_2Me)$ (?). *Methyl ether of colchicein* [145°]. Occurs in all parts of the meadow-saffron (*Colchicum autumnale*), especially in the seeds (Pelletier a. Caventou, *A. Ch.* [2] 14, 69; Geiger a. Hesse, *A.* 7, 274; Hubschmann, *Ar. Ph.* [2] 92, 330; Aschoff, *Ar. Ph.* [2] 89, 4; Bley, *Ar. Ph.* [2] 89, 18; Hubler, *C. C.* 1865, 536; Flückiger, *Ph.* [3] 7, 372; Hertel, *C. C.* 1881, 501; *Ph.* [3] 12, 498; Rosenwasser, *Ph.* [3] 8, 507; Houdès, *C. R.* 98, 1442; Zeisel, *C. R.* 98, 1587; *M.* 4, 162; 7, 557; 9, 1).

Preparation.—The whole seeds are extracted with hot 90 p.c. alcohol, and the residue digested with water. The aqueous solution is shaken with $CHCl_3$. On evaporation the chloroform leaves a syrupy residue, which after some days begins to crystallise. It is recrystallised repeatedly from alcohol and chloroform, and finally from water (Zeisel).

Properties. Yellowish-white powder. Sol. water and alcohol, insol. ether; darkens when exposed to the light. It is lævorotatory. Mineral acids colour the solution yellow. Weak alkalis also give a yellow colour; concentrated acids yield a yellow resinous pp. Conc. HNO_3 gives a violet colour. Conc. H_2SO_4 with a trace of nitrate gives a yellow green. Br water a yellow pp. Iodine in KI a brown pp. Fe_2Cl_6 no colour except on warming, when a green colour is produced. $HgCl_2$ in neutral solutions gives a slight turbidity, when acid a yellow pp. $AuCl_3$ yellow needles, CdI_2, potassium bismuth iodide, potassium mercuric chloride, phosphotungstic and phosphomolybdic acids, and chromates give yellow pps. Tannic acid in acid and neutral solution a white pp. It forms an addition compound with $CHCl_3$ of the formula $C_{22}H_{25}NO_6.2CHCl_3$ with evolution of heat. Yellow needles decomposed by water. Phenol gives a milkiness, and finally a yellow resin. Colchicine acts as a diuretic, purgative, and irritant poison (Mairet a. Combemale, *C. R.* 104, 439, 515).

Salts.—Colchicine is a weak base, most of its salts being decomposed by water. The aurochloride $B'HAuCl_4$ is stable.

Colchicein $C_{21}H_{23}NO_6$ *i.e.* $C_{15}H_9(OMe)_3(NHAc)(CO_2H)$. *Tri-methyl-acetyl-colchicinic acid* [c. 166°].

Preparation.—By warming an aqueous solution of pure colchicine with 2 p.c. H_2SO_4 or 1 p.c. HCl. Separates in white needles. There are also formed methyl alcohol, an acid substance, and a new or possibly two new bases.

Properties.—Shining white needles (containing ½ aq); becomes anhydrous at 140°–150°. Lævorotatory. V. e. sol. alcohol and chloroform, insol. ether and benzene. Sol. mineral acids giving a yellow solution, in the case of HCl with rise of temperature. Alkalis also dissolve it, yielding yellow solutions. Conc. H_2SO_4 and HNO_3 behave with it as with colchicine. Br water, phosphomolybdic acid and aqueous phenol yield slight pps. in the aqueous solution, but not other reagents. In HCl solution it behaves like colchicine with most reagents. From conc. HCl solution $AuCl_3$ ppts. an orange-gold compound, which can be subsequently crystallised in needles. Lead and copper acetates give pps. HCl converts it into the hydrochloride of tri-methyl-colchicinic acid $C_{19}H_{21}NO_5HCl$ which forms a Pt salt $(C_{19}H_{21}NO_5HCl)_2PtCl_4$ 2aq. The dimethyl-colchicinic acid and colchicinic acid are also produced.

Salts.—$B'HAuCl_4$.—$(C_{21}H_{22}NO_6)_2Cu$ 5aq (Zeisel, *M.* 7, 585; 9, 8).

Amide of colchiceïn $C_{21}H_{24}N_2O_5$ *i.e.* $C_{15}H_9(OMe)_3(NHAc)(CONH_2)$ (?). Formed when colchicine and alcoholic NH_3 are heated together in a sealed tube. After evaporating the alcohol a yellow crystalline mass is left, which is recrystallised from alcohol. Two kinds of crystals separate. Those which effloresce contain ½ mol. alcohol.

Properties.—Heated with NaHO it forms colchicein and NH_3. It behaves as a base, being sol. HCl, insol. water. Fe_2Cl_6 gives a brown colouration, and in HCl solution KNO_2 gives a violet colour, and the alkaloidal reagents give precipitates. Conc. H_2SO_4 dissolves it, giving a yellow-red colouration (Zeisel, *M.* 9, 26).

COLCHICINIC ACID $C_{16}H_{15}NO_5$ *i.e.* $C_{15}H_9(OH)_3(NH_2)(CO_2H)$ (?).

Preparation.—The hydrochloride remains in the mother-liquor after separating the dimethyl- and trimethyl-derivatives formed from colchicein by heating with HCl. After drying at 109° the colchicinic acid is obtained as a yellow powder.

Properties.—HCl solution is ppd. by Br water, KI, $HgCl_2$, $PtCl_4$, $AuCl_3$, CdI_2, and by the usual alkaloidal reagents. Phenol gives no pp. Conc. H_2SO_4 gives a brown colouration; if a nitrate be present, and then excess of NH_3 added, a red colour is produced. Fe_2Cl_6 gives a red-brown colouration (Zeisel, *M.* 9, 22).

Dimethyl-derivative $C_{18}H_{19}NO_5$. [142°]. The hydrochloride is formed with the trimethyl-derivative. It crystallises from hot water as $B'HCl$ aq, from which the free acid is obtained in yellow microscopic prisms by the addition of weak NaHO. These prisms contain 4½aq. A solution gives the usual alkaloid reactions (Zeisel, *M.* 9, 17).

Trimethyl derivative $C_{19}H_{21}NO_5$ *i.e.* $C_{15}H_9(OMe)_3(NH_2)(CO_2H)$? [150°]. From the hydrochloride formed from colchicein (*q.v.*). Microscopic prisms (containing 2 aq). It forms a Pt salt $(B'HCl)_2PtCl_4$ 2aq.

COLEÏN $C_{10}H_{10}O_5$ (?) A brittle red resin, which may be extracted by acidulated alcohol from the leaves of *Coleus Verschaffeltii* (Church, *C. J.* 31, 253).

COLLAGEN *v.* Proteïds, *Appendix C.*

COLLIDINE *v.* Tri-methyl-pyridine and Methyl-ethyl-pyridine.

COLLINIC ACID obtained by Fröhde (*J. pr.* 80, 344) by oxidising gelatin with CrO_3 is Benzoic acid.

COLLODION *v.* Cellulose.

COLLOIDS. Name given by Graham to those substances which do not diffuse through porous membranes. *Colloids* are contrasted with *Crystalloids.* *V.* Diffusion, and Physical methods.

COLLOTURINE *v.* Loturine.

COLOCYNTHIN $C_{56}H_{84}O_{23}$ (?) S. (cold) 5; (hot) 6·3. The bitter principle occurring in the pulp of the fruit of *Citrullus Colocynthis* (Vauquelin, *J. Phys.* 84, 338; Braconnot, *J. Ph.* 10, 415; Herberger, *Buchner's Repert.* 35, 368; Bastick, *Ph.* 10, 239; Walz, *Ar. Ph.* [2] 96, 141; 99, 338; Lebourdais, *A. Ch.* [3] 24, 58; Henke, *Ar. Ph.* [3] 21, 200).

Preparation.—The fruit is extracted with alcohol, the alcohol is evaporated, and the residue taken up by cold water; lead acetate is added, and in the filtrate, after removing the excess of lead by H_2SO_4, the colocynthin is ppd. by tannin. The compound with tannin is then decomposed by lead carbonate.

Properties.—Yellowish prisms or powder. Sol. water and alcohol, insol. ether, CS_2, benzene, chloroform, and ligroin. Conc. H_2SO_4 gives a red colouration. It easily reduces Fehling's solution. Boiling aqueous HCl gives a dark green greasy pp., and the solution still reduces Fehling's solution. According to Walz, colocynthin is split up by boiling dilute H_2SO_4 into glucose (2 mols.) and a resin colocynthein $C_{44}H_{64}O_{13}$.

COLOMBIN *v.* COLUMBIN.

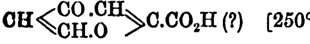
COLOPHENE. This name is applied by Armstrong and Tilden to the viscid yellow oil left after distilling all that is volatile in steam from the crude product of the action of H_2SO_4 on the terpenes. It is probably a mixture of polymerides of these hydrocarbons (*C. J.* 35, 748). Deville (*A. Ch.* [2] 75, 66; [3] 27, 85) applied the name to the portion of the product of the action of H_2SO_4 on French turpentine that boils a little above 300°. This might be called dicamphene, $C_{20}H_{32}$. A similar product occurs among the products of the distillation of colophony, but it differs from Deville's colophene in forming a grease when rubbed with slaked lime. *V. also* TERPENES.

COLOPHONY *v.* TERPENES and TURPENTINE.

COLUMBIC ACID $C_{21}H_{22}O_5$ aq? An acid which may be extracted by lime-water from Columbo root (Bodecker, *A.* 69, 47). Amorphous, nearly insol. water, v. sol. alcohol, sl. sol. cold ether.—$Pb_2A'_4Pb(OH)_2aq$?.

COLUMBIN $C_{21}H_{22}O_7$. [182°]. S. (alcohol) 3 at 78°. Occurs in the Columbo root (from *Menispermum palmatin*, together with berberin and a substance [220°] which crystallises from HOAc in prisms. Prepared by extracting the root with ether. On evaporation a crystalline residue, together with a fatty substance, separates out; the latter is removed by washing with ether, and the former crystallised from alcohol (Wittstock, *P.* 19, 298; Liebig, *P.* 21, 30; Röse, *P.* 19, 441; Bödecker, *A.* 69, 39; Paterno and Oglialoro, *G.* 9, 66; Alessandri, *Ph.* [3] 12, 995). Tastes very bitter. V. sl. sol. cold water, alcohol, and ether.

COMANIC ACID $C_5H_3O_2.CO_2H$ *i.e.*



$CH\genfrac{}{}{0pt}{}{\ll CO.CH}{\ll CH.O}\!\!>\!\!C.CO_2H$ (?) [250°].

Preparation.—1. Comenic acid (*q.v.*) is treated with PCl_5 and the di-chloro-comanic acid produced is reduced by HI (b.p. 127°) (Ost, *J. pr.* [2] 29, 62).—2. Chelidonic acid is heated *in vacuo* at 230° (Haitinger a. Lieben, *M.* 6, 279).

Properties.—Oblique prisms. Sl. sol. water. Gives no colour with Fe_2Cl_6.

Reactions.—1. Decomposed by excess of *baryta* with precipitation of the salt of an acid which gives a brown colour with Fe_2Cl_6. On warming the pp. with excess of baryta it changes to baric oxalate, acetone being evolved (compare chelidonic acid).—2. Heated by itself it splits up into CO_2 and $C_5H_4O_2$, pyrocomane, a neutral substance, insol. water, [32°] (c. 213°).—3. Warmed with conc. NH_3 it reacts thus (compare the behaviour of comenic and of oxy-comenic acids): $C_6H_4O_4 + NH_3 = C_6H_5NO_3 + H_2O$. The product is oxy-pyridine carboxylic (β-oxy-picolinic) acid $C_5H_3N(OH)(CO_2H)$.—4. When comanic acid (10 g.), *hydroxylamine hydrochloride* (6 g.), Na_2CO_3 (4·5 g.) and water (100 g.) are warmed together, the sparingly soluble oximido- acid separates $C_5H_3O(NOH).CO_2H$. Crystallised from water, it forms crystals which decompose at 200°. With fuming HCl at 200° this forms $C_5H_5NO_2$, a crystalline body that is very soluble in water. The oximido- acid is reduced by Zn and HCl to oxy-pyridine carboxylic acid. From this it would appear that the oximido- acid is di-oxy-pyridine carboxylic (di-oxy-picolinic) acid (H. Ost, *J. pr.* [2] 29, 378).—5. *Ethylamine* converts comanic acid into oxy-ethyl-pyridine-carboxylic (oxy-ethyl-picolinic) acid, $C_5H_2N(OH)(CO_2H)Et$. This acid splits up at 160° into CO_2 and (?) oxy-ethyl-pyridine.

Salts.—BaA'_2aq: v. sol. water. $BaA'_2 3aq$. AgA'.

Ethyl ether EtA'. [103°]. Prisms; not acted upon by AcCl.

Chloro-comanic acid $C_6H_3ClO_4$. [247°]. Formed, together with the following, from comenic acid by successive treatment with PCl_5 and water. Needles.

Di-chloro-comanic acid $C_6H_2Cl_2O_4$. [217°]. Needles (from alcohol). HI converts it into comanic acid.

COMBINATION, CHEMICAL, LAWS OF.—Chemistry concerns itself with the changes of composition and properties which certain definite kinds of matter undergo. Those kinds of matter which are studied in chemistry are divided into two classes, elements and compounds. Elements are those kinds of matter which undergo chemical change only by combining with other elements or compounds. Compounds may combine with other compounds or with elements, or they may be separated into two or more elements or compounds each unlike the others, and each weighing less than the original quantity of the compound used.

The expression 'homogeneous bodies' has sometimes been employed to denote elements and compounds, and to distinguish these from mixtures which palpably consist of unlike portions.

The law of the conservation of matter holds good in all chemical, as in all physical, changes. This law may be stated as follows as regards chemical occurrences:—*When homogeneous bodies interact to produce new bodies, the sum of the masses of the bodies produced is equal to the sum of the masses of those which have interacted to produce them.*

The proof of this law is found in the whole body of chemical and physical science. A few numbers are here given, taken from the researches of Stas, which were conducted with very great care and accuracy.

(1) Silver iodide is the sole product of the combination of iodine and silver; if the law of the conservation of mass holds good, the mass of silver iodide formed should be exactly equal to the sum of the masses of silver and iodine used.

Iodine used.	Silver used	Sum of Silver and Iodine.	Silver iodide formed	Differences.
32·4665	27·6223	60·0888	60·086	–·0028
46·8282	39·8405	86·6687	86·6653	–·0034
44·7599	38·0795	82·8394	82·8375	–·0019
160·2752	136·3548	296·6300	296·624	–·0060
96·7964	82·3631	179·1595	179·159	–·0005

The mass of silver iodide formed was in every case slightly less than the sum of the masses of silver and iodine used; but this is accounted for by the fact that it is impossible to collect absolutely the whole of the silver iodide formed. The differences amount to about $\frac{1}{20,000}$ of the total weight, and fall within the limits of necessary experimental errors.

(2) In another series of experiments Stas heated silver iodate, and so decomposed it into silver iodide and oxygen; the differences between the mass of iodate used and the sum of the masses of iodide and oxygen obtained amounted to about $\frac{1}{78,000}$ of the total weight. Here are a few of the results:—

Silver iodate	Silver iodide	Oxygen	Sum	Difference
98·2681	81·5880	16·6815	98·2695	+·0014
156·7859	130·1755	26·6085	156·7810	–·0019.

Homogeneous bodies interact to produce new homogeneous bodies in certain definite and fixed ratios; there is a constant ratio between the masses of the interacting bodies, and also between the mass of each interacting body and the mass of the product, or of each of the products, of the change.

The validity of this statement is assumed in all chemical investigations. Stas carried out a series of elaborate researches in order to determine whether the statement is or is not absolutely accurate. The following numbers taken from Stas' memoirs are illustrations of his results.

(1) Potassium chloride was caused to react with nitric acid to form potassium nitrate; the masses of potassium chloride and of potassium nitrate were determined.

Potassium chloride taken	Potassium nitrate formed	Potassium nitrate from 100 parts of chloride	Difference from mean
50·7165	68·6938	135·643	–·002
80·2610	108·8665	135·638	–·007
72·1022	99·8050	135·647	+·002
50·2175	68·1200	135·649	+·004
48·9274	63·3675	135·645	·000
69·8836	94·7900	135·640	–·005
14·2578	19·3415	136·655	+·010
		Mean 135·645	

The divergences from the mean are very small and are wholly accounted for by necessary experimental errors.

(2) A solution of silver was added to a solution of potassium bromide until the whole of the bromine was precipitated as silver bromide, and from the results was calculated the mass of potassium bromide which reacted with 100 parts by weight of silver. The numbers obtained established the absolute identity of the ratio of silver to potassium bromide in every experiment. Thus five experiments gave the following results:—

Potassium bromide	Silver	Potassium bromide reacting with 100 parts of silver	Difference from mean
9·20526	8·34305	110·332	–·008
20·12315	18·23665	110·313	+·003
15·8310	14·3151	110·357	+·017
11·0613	10·0253	110·334	–·006
16·3032	14·77495	110·335	–·005
		Mean 110·340	

The relations between the masses of interacting homogeneous bodies are expressed in the three laws of chemical combination, usually known as the law of fixity of composition, or the law of constant proportions; the law of multiple proportions; and the law of reciprocal proportions, or the law of combining weights. These laws may be stated in various forms of words; the following are fairly satisfactory.

Law of constant proportions. *The masses of the constituent elements of every compound stand in an unalterable ratio to each other, and also to the mass of the compound formed.*

Law of multiple proportions. *When two elements combine to form more than one compound, the masses of one of the elements which combine with a constant mass of the other element bear a simple relation to each other.*

Law of reciprocal proportions; or law of combining weights. *The masses of different elements which severally combine with one and the same mass of another element are also the masses of these different elements which combine with each other, or they bear a simple relation to these masses.*

When gaseous homogeneous bodies react to produce new gaseous bodies, the relations between the volumes of the interacting bodies and the volume of the product, or the volumes of the products, are expressed in the law of volumes or the law of Gay-Lussac.

Law of volumes. *When gaseous elements or compounds interact, the volumes of the interacting bodies bear a simple relation to each other, and also to the volumes of the gaseous products of the reaction.*

The law of constant proportions asserts the absolute invariability of the composition of every chemical compound. This law was finally gained as one result of the long controversy waged between Berthollet and Proust throughout the years 1801 to 1808. Many of the older chemists regarded every chemical compound as of fixed composition; the investigations of Bergmann and Lavoisier, for instance, implicitly assumed the validity of this law of fixity of composition. Indeed, even so far back as the middle of the 17th century Van Helmont spoke of the saturation-point which is reached when a definite quantity of an acid is added to a specified quantity of a base. The experiments of Richter in the last years of the 18th century rendered it probable that the masses of two acids, which severally neutralise one and the same mass of a given base, bear a constant ratio to each other independently of the nature of the base with which they react.

Berthollet, in his *Essai de statique chimique*, published in 1803, stated the fundamental law of chemical action, to the effect that the amount of a chemical change is dependent on the affinities and the masses of the reacting bodies. One of the conclusions which he drew from this generalisation was, that the composition of the products of a chemical reaction may vary within certain limits, which are determined by the relative masses of the interacting bodies, and by the physical states of these bodies, and of those produced in the change. Proust opposed this notion of variability of composition. He analysed with great care many series of compounds, chiefly metallic oxides and sulphides, and as a final result he established the law of fixity of composition, or of constant proportion, on a firm basis of experimentally determined facts.

Proust admitted that two elements might combine in more than one ratio. Indeed he analysed various pairs of oxides and sulphides of the same metal; for instance, he gave the following analyses of oxides of copper and of tin:—

Copper oxides			*Tin oxides*		
	(1)	(2)		(1)	(2)
Copper	= 86·2	80	Tin	= 87	78·4
Oxygen	= 13·8	20	Oxygen	= 13	21·6

Proust contented himself with stating the results of his analyses of compounds in percentages of the constituent elements. Had he calculated the masses of oxygen which were combined with the same mass of copper, or the same mass of tin, he might perhaps have forestalled Dalton and announced the law of multiple proportions. For Proust's analyses quoted above, if thus treated, give these results:—

Copper oxides			*Tin oxides*		
	(1)	(2)		(1)	(2)
Copper	= 86·2	86·2	Tin	= 87	87
Oxygen	= 13·8	21·5	Oxygen	= 13	24

Dalton analysed two compounds of carbon and hydrogen, and found that the ratio of carbon to hydrogen in one compound was twice that of carbon to hydrogen in the other; in other words, he found that a fixed mass of hydrogen combined with a definite mass of carbon to form one compound, and with twice that mass of carbon to form another compound. Dalton did not conduct the experiments which led to this result solely with the view of finding the quantitative laws of chemical combination, but rather with the object of rendering clear the atomic conception of chemical change which at this time was occupying his attention. While determining the composition of series of compounds, he had always in his mind the conception of chemical combination as consisting in the union of extremely minute portions of the combining bodies. These minute portions, or atoms, of an element, he pictured to himself as chemically indivisible, and as all of the same mass; hence, he argued, if two elements combine to form more than one compound, the masses of one of these elements which combine with a fixed mass of the other element must bear a very simple relation to each other, one must be a whole multiple of the other, because portions of atoms cannot combine, and all the atoms of the same element have the same mass.

The law of multiple proportions was a necessary consequence of the Daltonian atomic theory. As a matter of fact, the law was deduced from experimental data by reasoning directed by the mechanical conceptions of this theory (*v.* Atomic and molecular weights, vol. i. pp. 336–7). Dalton's analyses were not very accurate. There can be little doubt that it was not the analytical results which led him to the discovery of the law of multiple proportions, but that the law was tentatively deduced from the atomic conception he had formed of chemical processes, and was then confirmed by the results of his analyses of compounds.

The announcement of the law of multiple proportions at once threw a flood of light on the empirical data already amassed regarding chemical composition; and it also led to more careful analyses of numerous compounds, by showing the importance of these analyses, and by interpreting their results in terms capable of general application.

After the publication of Dalton's *New System of Chemical Philosophy* in 1808, chemists everywhere busied themselves with making accurate analyses of compounds. Some chemists accepted the atomic theory of Dalton, others preferred to speak of combining proportions, or equivalents, rather than of atoms, of elements; but whether accepting or rejecting his theory, all were influenced by Dalton's teaching. The development of the atomic theory and the verification of the laws of chemical combination are indissolubly bound together.

If the atomic theory were granted, not only the law of multiple proportions, but also that of reciprocal proportions, followed as a necessary consequence. For the masses of two or more elements which combine with each other must be the masses, or whole multiples, or submultiples, of the masses, of those elements which severally combine with a fixed mass of some other specified element; because combination occurs between atoms, and atoms are chemically indivisible, and all the atoms of any element are of the same mass.

The outcome of the researches of Berzelius and his followers into the composition of compounds was to establish the laws of chemical combination on a firm basis; but so intimately were those investigations connected with the development of the atomic theory, and with the controversies which attended that development, that many chemists who demurred to the theory were inclined to deny the absolute validity of the laws as expressions of fact, and to think that these laws must stand or fall with the theory which had first given them importance.

The results of the laborious researches of Stas[1] have shown that the laws of chemical combination by mass are perfectly accurate statements of facts which hold good in all chemical processes.

Some of the results obtained by Stas have been already given (p. 236). The following analyses of silver chloride, and of ammonium chloride, prepared by different methods, serve to show that the composition of each of these two compounds at any rate is absolutely fixed:—

Method of preparation of silver chloride	Grams of silver chloride obtained from 100 of silver
1. Ag burnt in Cl gas . .	132·842
2. Ag dissolved in HNO_3Aq, and ppd. by HCl gas .	132·847
3. Ag dissolved in HNO_3Aq, and ppd. by HClAq .	132·848
4. Ag dissolved in HNO_3Aq, and ppd. by NH_4ClAq .	132·842

The ammonium chloride analysed was prepared in four different ways:—

(1) Commercial salammoniac was dissolved in water and boiled with nitric acid to destroy organic matter; the liquid was decomposed by pure lime; the ammonia produced was led into water and then neutralised by hydrochloric acid; the ammonium chloride was sublimed in a stream of ammonia.

(2) Commercial sulphate of ammonia was heated with sulphuric acid, then boiled with nitric acid; the solution was treated in the same way as described in (1).

(3) A solution of potassium nitrite was mixed with potash, zinc-dust was added, and the liquid warmed; the nitrite was thus reduced to ammonia, which was led into water, and then neutralised by hydrochloric acid, the ammonium chloride was sublimed in an ammonia-stream.

(4) A part of the ammonium chloride prepared in (3) was sublimed *in vacuo*.

Weighed quantities of the different preparations were dissolved in water, and the quantity of silver required for the precipitation of all the chlorine was very accurately determined; experiments were conducted at different temperatures. A selection is given from the results:—

		Grams used	Silver used	Grams NH_4Cl decomposed by 100 grams silver
Specimen (1)	at 20°	11·79643	23·7843	49·598
	at 100°	39·62130	79·88613	49·5974
„ (2)	at 20°	11·80844	23·8086	49·597
	at 100°	13·40631	27·0277	49·602
„ (3)	at 20°	6·25216	12·60716	49·593
	at 20°	10·71756	21·6093	49·597
„ (4)	at 20°	13·5129	27·2129	49·598
	at 20°	6·2250	12·5523	49·592
			Mean	49·5968

One of the forms in which the law of reciprocal proportions may be stated is as follows: *The elements combine in the ratios of their combining weights, or in ratios which bear a simple relation to these.* By the combining weight of an element is here understood the smallest mass of that element which combines with unit mass of a standard element (*v.* COMBINING WEIGHTS OF ELEMENTS). Suppose the standard element were oxygen; then if the combining weight of an element were determined from analyses of different compounds of that element, all of which compounds contained oxygen, the law asserts either that the same value for the combining weight should be deduced from all the analyses, or that the different values found should bear a simple relation to each other. Stas proved the absolute accuracy of the law as regards silver, by determining the mass of this element combined with 16 parts by weight of oxygen in various compounds. The compounds chosen were, silver iodate, bromate, chlorate, and sulphate. Stas reduced these compounds to silver iodide, bromide, chloride, and sulphide, respectively, and then determined the amount of silver in these salts.

The following values were obtained for the mass of silver combined with iodine, &c., and 16 parts by weight of oxygen: (1) From analyses of iodide prepared by reducing iodate 107·928; (2) from analyses of bromide prepared by reducing bromate 107·921; (3) from analyses of chlorate prepared by reducing chloride 107·937; (4) from analyses of sulphide prepared by reducing sulphate 107·920. Stas further reduced potassium chlorate to chloride and then determined the mass of silver needed to precipitate the chlorine which was combined with 16 parts of oxygen in the original chlorate; he thus indirectly obtained a value for the combining weight of silver, meaning thereby the mass of this element which combines with that mass of chlorine which enters into union with 16 parts by weight of oxygen; the number found was 107·930. Another method which Stas used for testing the accuracy of the law of reciprocal proportions consisted in finding the ratio of the masses in which two elements united to form a binary compound, and also the ratio of the masses in which the same pair of elements were united in a compound formed by the addition of a third element to the first binary compound. Stas determined the ratio of silver to iodine in silver iodide and iodate, of silver to chlorine in silver chloride and chlorate, and of silver to bromine in silver bromide and bromate. The results proved the absolute accuracy of the law.

There can be no doubt as to the accuracy of the laws of chemical combination by weight. These laws are perfectly accurate statements of facts, and they hold good in every chemical change.

The law of combination of gaseous elements and compounds by volume, enunciated by Gay-Lussac, has not yet been subjected to so rigorous an examination as that which the laws of combination by weight have undergone.

The ratio of the volumes in which hydrogen and oxygen combine to form water was determined by Lavoisier, in 1783, to be 1·91:1. Other chemists stated the ratio to be approximately

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[1] *Recherches sur les rapports réciproques des poids atomiques* [1860]. *Nouvelles recherches sur les lois des proportions chimiques, sur les poids atomiques et leurs rapports mutuels* [1865]. A German translation of both memoirs was published in 1867, with the title *Untersuchungen über die Gesetze der chemischen Proportionen, über die Atomgewichten und ihre gegenseitigen Verhältnisse.*

2:1. In 1805 Gay-Lussac and Humboldt announced that the ratio was exactly 2:1, and in 1808 Gay-Lussac made the generalisation, which he based on numerous experiments, that the volumes of gaseous elements or compounds which combine to form gaseous products can be expressed by small whole numbers, and that the volume of the gaseous product of such combinations is either the sum of the volumes of the constituents or it bears a very simple relation ($\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, &c.) to this sum. Gay-Lussac's experiments showed, for instance, that 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia, and with 2 volumes of oxygen to form 2 volumes of nitrogen dioxide, &c.

Investigations have recently been made by Scott regarding the volumetric ratio in which hydrogen and oxygen combine to form water. The results (*v.* Scott, *Pr.* 1887. 398; *B.A.* 1887. 668; *N.* 37, 439) do not finally settle the ratio but they all tend to show that it is slightly less than 2:1, the most probable value being 1·997:1.

The laws of chemical combination are all included in the two statements:

1. The elements combine in the ratios of their combining weights, or in ratios which bear a simple relation to these.
2. The gaseous elements combine in the ratios of their combining volumes, or in ratios which bear a simple relation to these.

By *combining weight* is here meant the smallest mass of an element which combines with unit mass of some specified element taken as a standard; and by *combining volume* is meant the smallest volume of a gaseous element which combines with unit volume of some specified gaseous element taken as a standard.

The first statement has been amply verified by accurate experiments; the second does not yet stand on so firm an experimental basis.

In connexion with this article *v.* the articles ATOMIC AND MOLECULAR WEIGHTS; COMBINING WEIGHTS OF ELEMENTS; COMPOSITION, CHEMICAL; EQUIVALENTS; FORMULÆ. M. M. P. M.

COMBINING WEIGHTS OF THE ELEMENTS.—The laws of chemical combination by mass are expressed in the statement, *the elements combine in the ratios of their combining weights, or in ratios which bear a simple relation to these.* The term *combining weight* is here taken to mean the smallest mass of an element which combines with unit mass of a standard element. Hydrogen is adopted as the standard element; hence the practical definition of combining weight, as here understood, is the smallest mass of an element that combines with 1 part by weight of hydrogen. But many elements do not combine with hydrogen; it is therefore often necessary to make use of some element other than hydrogen as a standard.

All the elements except fluorine and bromine form oxides, and most of the elements combine with chlorine. These two elements, oxygen and chlorine, are therefore frequently used as standards of reference in determinations of combining weights.

Oxygen combines with hydrogen in two ratios (by weight), 8:1 and 16:1; but chlorine and hydrogen combine only in the ratio 35·5:1 (these values are given in round numbers). In accordance with the definition given above, the combining weight of oxygen is said to be 8, and the combining weight of chlorine to be 35·5. The combining weight of an element may then be taken to be the smallest mass of it which combines with 1 part by weight of hydrogen, or 8 parts by weight of oxygen, or 35·5 parts by weight of chlorine.

The same value is found for the combining weights of some elements which form both oxides and chlorides, whether the value is determined from analyses of the compounds with oxygen or with chlorine. Sodium and silicon are cases in point. But in some cases, one value is found for the combining weight of an element from analyses of its oxide, and another value from analyses of its chloride. Thus $\frac{127}{3}$ is the smallest mass of iodine that combines with 35·5 parts by weight of chlorine, but $\frac{127}{5}$ parts by weight of iodine combine with 8 parts of oxygen, and if the combining weight of iodine is deduced solely from analyses of its hydride, the value found is 127. So also, the smallest mass of nitrogen that combines with 1 part by weight of hydrogen is 4·66, but a compound of nitrogen and oxygen is known which is composed of 2·8 parts of nitrogen in union with 8 parts of oxygen.

Different values, then, are frequently obtained for the combining weight of an element according as the combining weight is determined in reference to hydrogen, chlorine, or oxygen, as the standard element. But the different values always bear a simple relation to each other. The following table presents the values found for the combining weights of a few elements; the ratios of the numbers are stated in the last column. Round numbers are given:—

	Combining weights referred to			Ratio of values
	H = 1	O = 8	Cl = 35·5	
Nitrogen . .	4·6	2·8	4·6	5:3:5
Potassium . .	--	9·75	39	1:4
Copper . .	63·2	31·6	31·6	2:1:1
Arsenic . .	25	15	25	5:3:5

If, then, we define combining weight solely in terms of hydrogen as unity, we can determine the combining weights only of a minority of the elements; if we admit the employment of oxygen and chlorine as standards of reference, we frequently arrive at different values for the combining weight of the same element. One primary object in determining combining weights is to find a basis for a system which shall represent the composition of compounds in formulæ, by showing the number of combining weights of each element which are combined to form that quantity of a specified compound which is represented by its formula. In order to frame a satisfactory system of notation, some compromise must be come to as to the meaning to be given to the term combining weight. The difficulty may be partly overcome by adopting as the combining weight of an element the least common multiple of the numbers which express the masses of the element that severally combine with 1 part by weight of hydrogen, 8 parts of oxygen, and 35·5 parts of chlorine. For instance, in the case of nitrogen, the L.C.M. of 2·8 and 4·66 is 14; and in the case of arsenic, the L.C.M. of 25 and 15 is 75.

The values thus obtained are usually adopted when it is desired to frame a fairly satisfactory definition for the term combining weight. These values are either the same as the atomic weights of the elements, or the latter are whole multiples of the former numbers. If a satisfactory and consistent system of notation is to be based on the combining weights of the elements, it is better to adopt for the combining weights values which are always identical with the atomic weights. The term combining weight of an element must then be taken to mean either the smallest whole number, or a whole multiple of the smallest whole number, divisible without remainder by each of the numbers that express the masses of the element which combine with 1 part by weight of hydrogen, 8 parts of oxygen, and 35·5 parts of chlorine, respectively. The following table exhibits the smallest masses of each element that combine with 1 part by weight of hydrogen, 8 parts of oxygen, and 35·5 parts of chlorine; it also shows the L.C.M. of these numbers, and the last column contains the whole number by which each L.C.M. must be multiplied in order to get the value used as the combining weight of the specified element in the ordinary chemical notation, which value is identical with the atomic weight of the element. (The values in the table in the next column are given in round numbers.)

The combining weight of an element is sometimes said to be the smallest mass of that element which enters into chemical combination with other elements, the smallest mass of hydrogen which combines chemically being taken as unity. But in order to give an exact meaning to the phrase, 'smallest relative mass of an element which enters into chemical combination with other elements,' it is necessary to add, 'to form a chemically reacting unit of a compound,' or some such expression as this. Now, the only conception of 'the chemically reacting unit of a compound' which has been put into an exact form capable of presentment in quantitative terms and of general application is that which arises from the application of the molecular and atomic theory to chemical occurrences; it is indeed the conception of the molecule. The definition of combining weight as 'the smallest relative mass of an element which enters into chemical combination with other elements' is essentially an atomic and molecular definition, although it is not couched in atomic and molecular language. For many years attempts were made to base a system of representing the composition of compounds on the combining weights of the elements without the help of the conceptions of atom and molecule. That mass of an element which combined with 1 part by weight of hydrogen, or 8 parts of oxygen, was sometimes taken as the combining weight of the element, and sometimes a multiple of this mass was proposed. But it was only when the atomic and molecular theory led the way that a satisfactory and consistent scheme of representing chemical composition was gained. The atomic weight of an element is always equal to, or is a whole multiple of, the least common multiple of the numbers that express the smallest masses of the element which combine with 1 part by weight of hydrogen, 8 parts of oxygen, and 35·5 parts of chlorine, respectively; the principles which guide chemists in their choice of the multiple are set forth in the article ATOMIC AND MOLECULAR WEIGHTS. If accurate values are to be found for the atomic weights of the elements, it is evident that the combining weights must be determined with the greatest care.

Element	Smallest mass of element that combines with			L.O.M. of these numbers	L.O.M. =at. wt. × n
	1 part by wt. of H	35·5 parts of Cl	8 parts of O		
					n
Aluminium	—	9	9	9	3
Antimony	40	24	24	120	1
Arsenic	25	25	15	75	1
Barium	-	68·5	31·25	68·5	2
Beryllium	—	4·5	4·5	4 5	2
Bismuth	—	69·33	41·6	208	1
Boron	—	3·66	3·66	3·66	3
Bromine	80	80	—	80	1
Cadmium	—	56	28	56	1
Cæsium	—	133	133	133	1
Calcium	—	20	20	20	2
Carbon	3	3	3	3	4
Cerium	—	35	35	35	4
Chlorine	35·5	—	8·875	35 5	1
Chromium	-	17·4	17·4	17·4	3
Cobalt	-	29 5	19·66	59	1
Copper	63·2	31·6	31·6	63 2	1
Didymium	- -	48	28·8	144	1
Erbium	- -	55·33	55·33	55·33	3
Fluorine	19	19	--	19	1
Gallium	—	23·3	23·3	23·3	3
Germanium	—	18 05	18·05	18·05	4
Gold	—	65·66	65 66	65 66	3
Hydrogen	—	1	1	1	1
Indium	—	37·8	37·8	37·8	3
Iodine	127	42 33	25 4	127	1
Iridium	—	48 15	32·1	96 3	2
Iron	—	18 66	18·66	18·66	3
Lanthanum	—	46 66	46 66	46·66	3
Lead	—	103 5	51·75	103·5	2
Lithium	—	7	7	7	1
Magnesium	—	12	12	12	2
Manganese	—	27 5	13 75	52	1
Mercury	—	100	200	200	1
Molybdenum	—	19·2	16	96	1
Nickel	—	29 3	29 3	29·3	2
Niobium	—	18·8	18 8	18 8	5
Nitrogen	4·66	4·66	2 8	14	1
Osmium	- -	47 75	23·775	47·75	4
Oxygen	8	8	- -	8	2
Palladium	—	26·5	26·5	26·5	4
Phosphorus	10·33	6·2	6 2	31	1
Platinum	—	48·5	48·5	48·5	4
Potassium	—	39	39	39	1
Rhodium	—	26	17 33	104	1
Rubidium	—	85·4	85·4	85·4	1
Ruthenium	—	26·15	26·15	26·15	4
Scandium	—	14 66	14·66	14·66	3
Selenion	39·5	19·75	13·33	80	1
Silicon	7	7	7	7	4
Silver	-	108	108	108	1
Sodium	—	23	23	23	1
Strontium	—	43·5	43·5	43·5	2
Sulphur	16	8	5·33	16	2
Tantalum	-	36·4	36·4	36·4	5
Tellurium	62·5	31·25	20 83	62 5	2
Terbium	- -	49·33	49·33	49·33	3
Thallium	—	68	68	68	3
Thorium	—	58	58	58	4
Tin	—	29·5	29·5	29·5	4
Titanium	—	12	12	12	4
Tungsten	—	30·66	30·66	30·66	6
Uranium	—	48	60	240	1
Vanadium	—	12·8	10 24	51·2	1
Ytterbium	—	57·66	57·66	57·66	3
Yttrium	—	29·66	29·66	29·66	3
Zinc	—	32·5	32 5	32·5	2
Zirconium	—	22·5	22·5	22·5	4

The exact definition to be given to the term combining weight is not a matter of paramount importance, for it is evident that whether we call the combining weight of an element the smallest mass of it which combines with 1 part by weight of hydrogen, or 8 parts of oxygen, or 35·5 parts of chlorine, or whether we say that the combining weight is the L.C.M. of these numbers, or whether we take the expression to mean a whole multiple of this L.C.M., in any case the law holds good that the elements combine in the ratios of their combining weights or in ratios which bear a simple relation to these. What is required to be determined with the greatest care and accuracy is the ratio between the combining masses of every element and hydrogen, oxygen, chlorine, or other standard element; because this ratio, taken in conjunction with the definitions of atom and molecule, determines the value of the atomic weight of the element, and on this value depend many of the chemical properties of the element. In connexion with this article *v.* the arts. ATOMIC AND MOLECULAR WEIGHTS; COMBINATION, CHEMICAL, LAWS OF; FORMULÆ; NOTATION. M. M. P. M.

COMBUSTION.—Any manifestation of chemical energy attended by combination and accompanied by production of much heat is, strictly speaking, an instance of combustion. As commonly used, however, the term carries with it the idea of *incandescence*; that is, the reacting bodies are not merely *incalescent*, but have their temperature raised to a point at which they emit light, or become self-luminous. This definition includes that of *inflammation*, which is, however, best restricted to instances of combustion in which the incandescent substances are gaseous. Such cases of combustion will be considered under FLAME.

All phenomena of burning are instances of combustion, and in the great majority of cases they consist in the union of the oxygen of the air with the substance which is being burnt, the visible signs of combustion, *i.e.*, the heat and light, being the result immediate or proximate of the chemical energy so expended.

It has been frequently observed that primitive communities regard as sacred all things that contribute to their existence or promote their well-being, and hence it is intelligible that a phenomenon so mysterious in its origin and process as fire, and at the same time so necessary to the welfare of mankind, should have been looked upon from the earliest times with particular reverence and awe. The evidence of fire worship is to be found probably in every religion. And it would be easy to show on strictly evolutionary principles how the idea of sanctity associated with the phenomenon of burning ramified and became interwoven into theories of the origin of life, of generation, and the nature of the soul and mind, and how it passed into the art of healing, and thence into the sciences which have sprung out of, or have been grafted on to, that art. The idea, but little shorn of its transcendental and spiritual attributes, is to be found in the earliest theories of chemistry. Fire plays such an important part in the operations of chemistry, the changes which it induces are so profound and extraordinary, burning and the evolution of heat by intrinsic agencies are so constantly witnessed as the result of chemical operations, that it is hardly surprising that the earlier chemists should have regarded combustion as the essential phenomenon of chemistry. A theory of combustion was to them also a theory of chemistry. Minds so sharply contrasted as those of Bacon and Boyle clearly apprehended the importance of a comprehensive theory of combustion from this point of view, but Bacon made no attempt to construct such a theory, and Boyle, in spite of his habitual caution, went singularly wrong in his efforts to explain the essential nature of fire and the phenomena we now recognise as due to oxidation. John Joachim Becher (1635-1682) has the credit of having first attempted to group all the facts of chemistry then known in such manner that they could be deduced from one general or universal principle. George Ernest Stahl (1660-1734) eagerly adopted Becher's fundamental idea, and amplified and worked it into a comprehensive system, capable of wide generalisation and fruitful of fresh lines of investigation. The theory of Becher and Stahl was essentially one of combustion. As it has exercised a very powerful influence on the development of chemistry, it may be desirable to sketch its main features with some degree of detail.

The theory as elaborated by Stahl is to be found in his *Fundamenta Chymiæ*, published in 1720, when its author was resident at Berlin as physician to the King of Prussia. It is not improbable that it was taught publicly at Halle between 1694 and 1716 when Stahl was Professor of Medicine at that University. Stahl defines chemistry as the art of resolving compounds into their constituents, and of recombining these constituents to again form the original or other compounds. According to Becher and Stahl, all combustible bodies are compounds, and in the act of burning they part with a constituent which is common to them all. This common principle was termed by Stahl *phlogiston* (φλογιστός = burnt). Bodies are combustible in proportion as they contain phlogiston; phosphorus, sulphur, charcoal, alcohol, sugar, the oils, resin, &c., are pre-eminently endowed with it. The metals also contain it, but in varying amount. When certain of the metals are strongly heated they are gradually converted into an earthy powder, termed a *calx*. The change which the metal had undergone was considered by Stahl as akin to ordinary combustion, and metals were regarded as compounds of calces, which were recognised as intrinsically dissimilar bodies, in union with the common principle, phlogiston, which was dissipated by the action of heat upon the metal. The re-conversion of the calx into the metal by processes which we now term reduction, that is by the action at a sufficiently high temperature of bodies like charcoal, coal, or by combustible gases, &c., was explained by Stahl as being due to the union of the phlogiston of the charcoal, &c., with the calx of the metal. It was noticed that many substances like phosphorus and sulphur on being burnt formed acids which when treated with a highly phlogisticated body such as charcoal gave rise to the original substances. Thus, phosphoric acid on being heated to a high temperature with charcoal formed phosphorus again. Hence phosphorus was considered to be a compound of phosphoric acid and phlogiston; in the act of burning the phlogiston was disengaged and the acid left; on restoring phlogiston to the acid the phosphorus was regenerated. Stahl sought to demonstrate the identity of the combustible principle in all substances by pointing to the fact that the calx of lead, for example, could be converted into the metal by the employment of phlogisticated bodies of such widely different properties as charcoal, sulphur, flour, sugar, iron, &c. As only one substance, viz., lead, was formed by the action of each of these bodies, it seemed to follow that they must all contain a common principle. In the same way it was pointed out that phosphoric acid could be changed into phosphorus by the action of a great variety of combustible bodies, such as lamp-black, resin, sugar, or even the metals. Of course it was known that many substances existed which were incombustible and were not sensibly changed by the action of fire, as, for example, lime, clay, rocks, &c.; such bodies were regarded as dephlogisticated by the action of previous heat, or as being incapable of combining with phlogiston. As the doctrine of phlogiston extended, the ideas of the phlogistic school respecting its essential nature became more and more vague. There seems to be no doubt, however, that Stahl and his immediate followers, Neumann, Pott, and Margraaf, in Germany, and Réaumur, Duhamel, and Macquer, in France, regarded phlogiston as a definite substance possessing all the essential attributes of matter. Stahl himself appears to have considered that phlogiston, when isolated, would turn out to be a solid earthy body insoluble in water like charcoal, sulphur, phosphorus, bitumen, and the metals. Indeed, as so many highly phlogisticated bodies were insoluble in water, while their dephlogisticated constituents, *e.g.*, phosphoric and sulphuric acids, were readily soluble, the property of solubility came to be regarded as dependent on or related to the presence or relative amount of phlogiston. Its presence or absence in fact affected all the properties of bodies, and caused all the changes they were capable of experiencing, as, for example, their relative stability, their capacity for union with other bodies, their acid or caustic characters, their colour, odour, and taste, and even their physiological and therapeutic activity. Many other natural phenomena, such as fermentation and decay, the growth of plants, and the processes of animal life, were also capable of explanation by the aid of the same general principle.

The doctrine of phlogiston was of incalculable service to chemistry. Indeed, it is not too much to say that Stahl's generalisation first raised chemistry to the dignity of a science. It not only served to present a simple and intelligible explanation of a mass of hitherto unconnected facts, but it pre-eminently fulfilled the function of every fruitful hypothesis by stimulating fresh inquiry and suggesting new lines of thought. Men like Black and Cavendish, whom we commonly reckon as phlogistians, were, however, not unmindful of its weaknesses, and Black certainly recognised its inadequacy to explain facts which he knew to be incontrovertible, such, for example, as the results obtained by Boyle on the calcination of metals. Boyle himself was doubtless aware of the doctrine in the form in which it was presented in Becher's *Physica Subterranea*, but it had probably no influence on his labours. Indeed he failed to perceive that much of his work was in direct opposition to Becher's teaching. His experiments on the calcination of lead and tin were interpreted by him as proving the materiality of heat, and it was reserved for Lavoisier and the so-called antiphlogistic school of French chemists to point out their real significance.

The doctrine of phlogiston was paramount in chemistry for upwards of half a century: the discovery of nitrogen by Rutherford in 1772, and of oxygen by Priestley in 1774, and the fuller recognition of the functions of these bodies in the air, by paving the way towards a clearer apprehension of the nature of combustion, brought about the downfall of Stahl's generalisation. Geber, upwards of ten centuries ago, had supplied chemistry with facts respecting the nature of calcination which the long subsequent labours of Sulzbach, Cardan, Rey, and Boyle had confirmed and strengthened. Hooke, in the *Micrographia*, and Mayow, in his *Opera Omnia Medicophysica*, pointed out that combustion consists in the union of something with the body which is being burnt, and Mayow, both by experiment and inference, demonstrated in the clearest way the analogy between respiration and combustion, and showed that in both processes one constituent only of the air is concerned; he distinctly stated that not only is there increase of weight attending the calcination of metals but that this increase is due to the absorption of the same *spiritus* from the air that is necessary to respiration and combustion. Mayow's experiments are so precise, and his facts so incontestable, that, as Chevreul has said, one is surprised that the truth was not fully recognised until a century after his researches. This recognition was forced upon the world by the experimental labours and writings of Lavoisier and his immediate followers in France. By repeating and extending the observations of Mayow, Black, Rutherford, and Priestley, Lavoisier proved that respiration, combustion, and calcination are essentially identical processes, in that they are primarily due to the action of oxygen—Priestley's dephlogisticated air—on the body undergoing change, and that the heat which is manifested is the result of the chemical change of which all these processes are examples. Lavoisier's experiments were so well devised and so admirably executed, his reasoning was so perspicuous and his proofs so irrefragable, that his conclusions seemed irresistible so far as the theory of combustion was concerned.

As Lavoisier's explanation of the true nature of combustion effected a complete revolution in the theory of chemistry, it may be desirable to trace the steps by which he was led to formulate it.

Lavoisier published in all some sixty memoirs, about half of which were concerned with the subject of combustion and of matters which immediately grew out of it. These appeared in different memoirs of the Academy between 1774 and 1788. It appears from his collected memoirs, published after his death in 1794, that his earliest experiments on the cause of the augmentation of weight which bodies experience during combustion and calcination were made in 1772.

In a memoir published in 1774 Lavoisier described a repetition of Boyle's experiments on the calcination of tin, in which he showed that during the formation of the calx a portion of the air disappears, and that the tin increases in weight in amount equal to the loss of weight experienced by the air. Hence he concluded that a portion of air had united with the tin, and that the calx of tin is composed of tin and air.

There is nothing in this memoir nor in the note of 1772 to indicate that Lavoisier had any idea of the compound nature of air. Still it is evident that he had advanced beyond the position of Boyle and Rey. Boyle inferred that his experiments proved the materiality of heat, while Rey appears to have imagined that the absorbed air was merely entangled with the metal.

In the autumn of 1774 Priestley exhibited to Lavoisier his method of making oxygen gas from the calx of mercury. In the following year appeared Lavoisier's memoir *On the nature of the principle which combines with the metals during their calcination and which augments their weight*. Starting from the fact that many of the metallic calces can be reduced by charcoal with the production of a gas which is identical with that produced by burning charcoal in the air, Lavoisier concluded that carbonic acid gas contains an elastic principle which is common to the air and the metallic calx. In the case of the calx of mercury he could obtain this elastic principle by heat alone. The gas so obtained was identical with Priestley's dephlogisticated air. Lavoisier surmised that this gas, which he, like Priestley, found to be pre-eminently a supporter of combustion and respiration, was probably contained in nitre, inasmuch as this salt when heated with charcoal forms large quantities of carbonic acid gas. Mayow, on other grounds, had already made the same supposition. This memoir was followed in 1777 by that *On the combustion of phosphorus and the nature of the acid which results from that combustion*, in which Lavoisier first distinctly recognised that the air was composed of two distinct substances, one of which was absorbed by the burning phosphorus to the extent of one-fifth of the original volume of air, while the other, originally termed by him *mouffette atmosphérique*, was incapable of supporting combustion or animal life, and was not absorbable by metals when heated, and hence was not concerned in the process of calcination. In the same year he published a paper *On the combustion of candles in atmospherical air, and in air eminently respirable*, in which he demonstrates that the *mouffette atmosphérique*, or *azote* as it is now called, plays no part in the burning of the candle, but that the combustion is entirely due to the dephlogisticated air or oxygen. Although Lavoisier's theory of combustion and of calcination was now practically complete, and was fully developed by him in his memoir *On combustion in general* in 1778, it made comparatively little impression even in France, and gained no converts of note until 1785, when Berthollet and Fourcroy gave in their adhesion to the new doctrine. The death-blow to phlogiston really came from the discovery of the compound nature of water. It was only after Cavendish's experiments on the combustion of hydrogen that Lavoisier was able to combat the generally received opinion as to the nature of the process of solution of metals in acids. It was observed that when certain metals were dissolved in acids, hydrogen was evolved, and the metals were converted into calces which could be again transformed into the metals by heating in hydrogen. These facts were accounted for by the Stahlian hypothesis on the assumption that the gas evolved on the solution of the metal was actually phlogiston, and that on heating the calx with the gas the phlogiston again combined with it to regenerate the metal. In 1783 Lavoisier was informed by Blagden, who at that time acted as Cavendish's assistant, of the experiments of the latter, made in 1781, on the production of water by the combustion of hydrogen. The importance of the discovery of the true chemical nature of water was at once perceived by Lavoisier. He and Laplace repeated Cavendish's experiment in presence of Le Roi and Blagden, and found that water was composed of 1 vol. of oxygen and 1·91 vol. of hydrogen. Further evidence of the compound nature of water was obtained by passing steam over red-hot iron contained in a porcelain tube, when free hydrogen was formed together with a calx of iron. Lavoisier was now able to explain the origin of the hydrogen in the act of solution of a metal in a dilute acid, on the assumption that in the process water was decomposed, and that the oxygen united with the metal to form the calx, while the hydrogen escaped in the free state. This view is further developed in the memoir *On the solution of the metals in acids*, published in 1785. Finally, in an elaborate paper *On Phlogiston*, Lavoisier connects together his various observations, elaborates his own theory of combustion, and confutes the phlogistic hypothesis.

Whatever may be thought of Lavoisier's claims to be considered the discoverer of oxygen, and of the true nature of air and water, there can be no question as to his merit in being the first to recognise the relation of these discoveries to the theory of combustion. As far back as 1772 he seems to have been fully persuaded of the insufficiency of the Stahlian hypothesis, and for upwards of a dozen years he laboured, practically alone, to demonstrate its insufficiency. His triumph was complete in 1785, and *La Chimie Française*, as the new doctrine was termed by Fourcroy, was embraced in France with all the fervour of revolution. Nor did national prejudice long delay its adoption in Germany and Great Britain. The Berlin Academy pronounced against phlogiston in 1792. Black early became a convert, but both Cavendish and Priestley, in spite of the fact that their discoveries had contributed so largely to its downfall, remained faithful to Stahl's doctrine to the end—an exemplification of the truth of Priestley's words that 'We may take a maxim so strongly for granted, that the plainest evidence of sense will not entirely change, and often hardly modify, our persuasions; and the more ingenious a man is, the more effectually he is entangled in his errors, his ingenuity only help-ing him to deceive himself by evading the force of truth.'

T. E. T.

In connexion with Combustion *v.* OXIDATION and DEOXIDATION.

COMENAMIC ACID *v.* DI-OXY-PYRIDINE CARBOXYLIC ACID.

OXY-COMENAMIC ACID *v.* TRI-OXY-PYRIDINE CARBOXYLIC ACID.

COMENIC ACID $C_6H_4O_5$. S. above 6 at 100°. Got by boiling meconic acid $C_7H_4O_7$ with HCl, CO_2 coming off. Purified by crystallising the difficultly soluble ammonium salt from water (How, *A.* 80, 65; *Ed. Phil. Trans.* 20 [2] 225; *cf.* Robiquet, *A. Ch.* [2] 51, 326; 53, 428; Liebig, *A.* 7, 237; 26, 116; Stenhouse, *P. M.* [3] 25, 196). Comenic acid is thrown down as a white powder when HCl is added to a solution of its ammonium salt.

Properties.—Prisms, laminæ, or granules; sol. boiling water, insol. alcohol. At 260° it splits up into CO_2 and pyromeconic acid. Fe_2Cl_6 gives a red colour. Does not react with hydroxylamine (Odernheimer, *B.* 17, 2081).

Reactions.—1. *Sodium-amalgam* reduces it to syrupy hydrocomenic acid $C_6H_8O_5$, which forms a salt $Ag_2C_6H_6O_5$ (v. Korff, *A.* 138, 191).—2. If comenic acid is boiled with PCl_5 (4 equivalents) and $POCl_3$ until no more HCl comes off, and the liquid distilled till the thermometer reaches 150°, an oil remains in the retort which is converted by boiling water into di-chloro-comanic acid, $C_5HCl_2O_2.CO_2H$ (yield, 20 p.c.). It crystallises from alcohol in needles, [217°]. Some chloro-comanic acid, $C_5H_2ClO_2.CO_2H$, [247°] is formed at the same time. Both acids are reduced by boiling conc. HI to comanic acid, $C_5H_3O_2.CO_2H$ (*q.v.*). When comanic acid is boiled with aqueous NH_3 it is converted into (β)-oxy-picolinic (oxy-pyridine carboxylic) acid. 3. Heated with PCl_5 at 280° it gives C_5Cl_8 or 'perchloro-mecylene,' and hexachloro-ethane. Perchloro-mecylene crystallises from alcohol in compact oblique prisms, melting at [39°] (Ost, *J. pr.* [2] 27, 294). -4. *Ethylamine* gives di-oxy-ethyl-pyridine carboxylic acid, $C_5HEtN(OH)_2CO_2H$.—5. *Aniline* gives similarly di-oxy-phenyl-pyridine carboxylic acid (H. Ost, *J. pr.* [2] 29, 380).

Salts. — NH_4HA''aq: four-sided prisms; reddens litmus. V. sol. boiling water.—K_2A'': sl. sol. water.—KHA'': short square needles; reddens litmus. — $NaHA''$: four-sided prisms (from hot water).—BaA''aq (at 121°).—BaA''5aq: insol. boiling water.—$BaH_2A''_2$ 6aq: sol. water.—CaA''aq (at 121°).—$CaA''6\frac{1}{2}$aq: prisms, insol. water.—$CaA''3\frac{1}{2}$aq.—$CaH_2A''_2$ 7aq: crystals, v. sol. hot water. — $MgA''5\frac{1}{2}$aq: crystalline grains. — $MgH_2A''_2$ 8aq. — CuA''aq (at 100°).—$Fe(OH)H_2A''_2$ 2aq (at 100°).—PbA''aq.—$AgHA''$: granular pp.—Ag_2A'': thick yellow pp.

Ethyl ether $C_5H_2O_2(OH).CO_2Et$. [135°] (How); [127°] (Reibstein). From an alcoholic solution of the acid and HCl. Formed also by heating meconic acid with EtI and alcohol at 100°. Needles, v. sol. hot water. May be sublimed. Fe_2Cl_6 gives a red colour. Very readily saponified. By successive treatment with sodium-amalgam and chloroformic ether a compound $C_{11}H_{12}O_7$ [87°] may be got (Drechsel, *J. pr.* [2] 17, 164).

Acetyl derivative of the ether $C_5H_2O_2(OAc)(CO_2Et)$. [104°]. From the above and Ac_2O at 150° (Reibstein, *J. pr.* [2] 24, 277).

Ethyl derivative $C_5H_2O_2(OEt)CO_2H$. [240°]. Obtained by fusing the ethyl derivative of meconic acid (*q. v.*) by itself. Crystallised from water, animal charcoal being used, it forms long white needles (Mennel, *J. pr.* [2] 26, 458).

Salt.—$AgA'2\frac{1}{2}$aq: white needles.

Amide $C_5H_2O_2(OH)(CO.NH_2)$. Formed by passing NH_3 into an ethereal solution of ethyl comenate. A pp. of $C_5H_2O_2(ONH_4)CO_2Et$ is first formed, but this is then slowly converted into $C_5H_2O_2(ONH_4)CO.NH_2$, whence HCl liberates the amide. White plates (from water). Not affected by boiling water. Boiling NaOH converts it into sodic comenate. Its aqueous solutions give a red colour with Fe_2Cl_6.

Salt.—$C_5H_2O_2(OK)(CO.NH_2)$ aq. Insol. alcohol.

Chloro-comenic acid $C_5HClO_2(CO_2H)(OH)$ $1\frac{1}{2}$aq. Formed by passing Cl into water in which powdered comenic acid is suspended (How, *Ed. Phil. Trans.* 20 [2] 225). Four-sided prisms (from water). More soluble in water than comenic acid, v. e. sol. warm alcohol.—Ag_2A'' (at 100°).—$AgHA''\frac{1}{2}$aq.

Bromo-comenic acid $C_5HBrO_2(CO_2H)OH$. Formed by the action of bromine-water on comenic or meconic acids. Four-sided prisms; less soluble than the preceding body. Boiling baryta-water gives oxy-comenic acid.—$AgHA''$ (at 100°).—$AgHA''\frac{1}{2}$aq.

Ethyl ether EtA'. [141°]. From silver bromo-comenate and EtI. Glittering needles (Mennel, *J. pr.* [2] 26, 472).

Di-bromo-comenic acid

$C_5HBrO_2(OBr)(CO_2H)$ (?).

Formation.—From Br and bromo-comenic acid.

Preparation.—Meconic acid (10 g.) is suspended in water (80 g.) and bromine (18 g.) is added. The product separates at once as crystalline plates (containing 3aq).

Properties.—Its solution gives no colour with Fe_2Cl_6 in the cold, a red colour appears on heating, bromo-comenic acid being formed. At 105° the crystals give off Br (2 mols.) and H_2O. An aqueous solution of the acid gives no pp. with $BaCl_2$, but on adding NH_3 a red colour and an orange pp. are got. Zn and HCl reduce it to bromo-comenic acid.

Constitution.—This acid is not a true di-bromo-comenic acid, nor a compound of comenic or bromo-comenic acid with HBrO, hence it probably contains bromine in hydroxyl, although this is very unusual (Mennel, *J. pr.* [2] 26, 466).

Ethyl ether $C_5HBrO_2(OBr)(CO_2Et)$. From mono-ethylic meconate (10 g.), water (80 g.) and bromine (18 g.). Small yellowish tablets (containing 2aq). Sol. water, alcohol, and ether. Readily decomposes. When heated with water or with SO_2 it changes to white needles of bromo-comenate of ethyl [141°] (*v. supra*).

Nitro-comenic ether $C_5H(NO_2)(OH)CO_2Et$. [147°]. From HNO_3 (S.G. 1·5) and comenic ether in the cold. Better by passing N_2O_3 into an ethereal solution of ethyl comenate (R.). Sol. hot water, alcohol, and ether. Its aqueous solutions give with Fe_2Cl_6 a red colouration.

Salts.—$C_5H(NO_2)(ONa)CO_2Et$. Yellow needles. Explodes when heated.—$\{C_5H(NO_2)CO_2Et\}_2O_2Ba$. Explodes when heated. Silver salt blackens even when cold.

Amido-comenic acid $C_5H(NH_2)O_2(OH)CO_2H$. Formed by reduction of nitro-comenic ether by Sn and HCl (R.). Slender silky needles (containing aq) (from water). Sl. sol. alcohol and ether. Its aqueous solutions give a blue colour with a little Fe_2Cl_6, more Fe_2Cl_6 turns the liquid red.

Salt.—$C_5H(NH_2)O_2(OH)CO_2H,HCl,3aq$. Glittering scales, formed by adding conc. HCl to the above. Decomposed by water, losing HCl.

Oxy-comenic acid $C_5HO_2(HO)_2CO_2H$. From bromo-comenic acid by boiling baryta, or with HCl (R.). Also from comenamic acid, $KMnO_4$, and dilute H_2SO_4. Crystallises from water in long needles (with 3aq) or in short prisms (with aq). V. sol. water and alcohol, sl. sol. ether. In its aqueous solution Fe_2Cl_6 gives a blue colour turned red by excess. NH_3 at 100° gives tri-oxy-pyridine carboxylic acid.

Salts.—$C_5HO_2(HO)_2CO_2NH_4$.—$\{C_5HO_2(OH)_2CO_2\}_2Ba, 2aq$.—$C_5HO_2(OK)_2CO_2K$.

Ethyl ether $C_5HO_2(HO)_2CO_2Et$. [204°]. Small prisms (from alcohol).

Di-acetyl derivative of the ether $C_5HO(OAc)_2CO_2Et$. [75°]. Small needles (from alcohol).

COMPOSITION, CHEMICAL. By the chemical composition of a compound is meant, primarily, a statement of the masses of the elements by the combination of which a specified mass – say 100 parts—of the body has been produced, or into which a specified mass of the body may be resolved. So long as nothing more than the percentage elementary composition of compounds was determined, chemistry remained a collection of unclassified facts. The establishment of the law of multiple proportions, and the development of this law, and also that of combining weights, led to the possibility of assigning to each compound a certain number which expressed the smallest relative mass of it that entered into chemical reactions with other compounds; but no generally applicable method for determining the values of these chemically reacting masses was found until the help of the atomic and molecular theory had been sought (*v.* COMBINATION, CHEMICAL, LAWS OF; and COMBINING WEIGHTS OF ELEMENTS). The composition of the smallest chemically reacting mass is expressed by the formula of the compound, which tells the number of combining weights of each elementary constituent which have combined to form the mass in question. This wider meaning of chemical composition rests on, and arises from, the laws of chemical combination; but it became definite only when supplemented by atomic and molecular conceptions.

The atomic weights of all the elements have been determined with more or less accuracy; when the molecular weight of a compound is known, the chemical composition of that compound is expressed in a formula which states the number of atoms of each element that have combined to form a molecule of the compound (*v.* ATOMIC AND MOLECULAR WEIGHTS). In this further widening of the conception of chemical composition, the properties of a compound are represented as determined by the nature and number of the atoms which form the molecule of the compound. This conception rests on, and arises from, the molecular and atomic theory.

It frequently happens, especially among compounds of carbon, that two or more compounds have the same composition and the same molecular weight, and yet differ in properties; such compounds are said to be isomeric. These differences in properties are generally regarded as associated with differences in the arrangement or configuration of the atoms which form the molecules of the compounds in question. More or less conventional methods are used for expressing the supposed relations between the properties of isomeric compounds and the structures of their molecules. These methods are based on the hypothesis of atomic valency which has arisen from the application of the molecular and atomic theory to the study of isomerism (*v.* EQUIVALENCY; FORMULÆ; ISOMERISM).

The term *chemical constitution* (*q.v.*) is often used to express that conception of chemical composition which includes an attempt to exhibit the properties of a compound as determined not only by the nature and number, but also by the relative arrangement, of the atoms which form the molecule of the compound.

In the preceding paragraphs it has been assumed that the composition of every element is always the same. As a matter of fact many bodies which were once regarded as elements have been proved to be compounds; and recent researches show that this process is likely to be repeated on some of those kinds of matter which are now classed among the elements. Be this however as it may, it is certain that some elements exhibit different properties when they are obtained from their compounds under different conditions. Phosphorus, carbon, oxygen, sulphur, and several other elements, exist in more than one form; they exhibit the phenomenon of allotropy. What we have learned of the connexions between properties and composition shows that these differences in properties are to be regarded as associated with differences in composition. The only consistent conception which can be formed at present of variations in the composition of elements is that which is furnished by the molecular and atomic theory According to this conception, the properties of an element depend not only on the nature of its atoms, but also on the numbers of these atoms which are combined to form a molecule, and on the relative arrangement of the atoms in the molecule (*v.* ALLOTROPY, vol. i. p. 128).

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COMPOUND RADICLES. The study of chemical composition and properties has led to the conception that certain groups or collocations of atoms in the molecules of various compounds remain so closely associated throughout chemical changes which the molecules undergo, that the functions performed by those groups of atoms in these reactions are practically identical with the functions performed by elementary atoms. Such groups of atoms are called *compound radicles* in distinction to the atom of an element which may be called a *simple radicle*. When two elements combine we may say that the compound is formed of two simple radicles;

e.g. NaCl is formed of the radicles Na and Cl; when two compounds combine to form what is generally called a *double compound* or a *double salt*, which double compound is easily resolved into the compounds by whose union it was formed, we may say that the double compound is formed of two compound radicles, each of which can be isolated. Similarly, when a compound goes through a series of reactions with the production of new compounds, all of which contain certain elements of the original compound, we may suppose that these certain elements were in some way closely associated in the original compound, and although we cannot isolate this group of elements, yet we may advantageously regard the original compound and those produced from it as formed by the union of this collocation of elementary atoms, or this compound radicle, with other atoms. The conception of the compound radicle is only a widening of the conception of the element; it is closely associated with the subjects of *chemical classification* and *chemical constitution* (*q.v.*). In connection with this subject *v.* Radicle and Types, vol. iv.

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CONCHIOLIN *v.* Proteids, *Appendix C.*

CONCUSCONIDINE *v.* Cinchona bases.

CONCUSCONINE *v.* Cinchona bases.

CONESSINE $C_{12}H_{20}N$. [121½°]. Probably identical with *wrightine* (Stenhouse, *Ph.* [2] 5, 493; Haines, *Ph.* [2] 6, 132; Warnecke, *Ar. Ph.* [3] 26, 248, 281), which occurs in the bark and seeds of *Wrightia antidysenterica*, called conessi bark; occurs in the bark of *Holarrhena africana* (P. a. S.), and (though in much smaller quantity) in the East-Indian *H. antidysenterica* (Polstorff, *B.* 19, 1682). White silky needles. V. sol. alcohol, ether, benzene, and chloroform, v. sl. sol. water. Very bitter taste. Scarcely volatile with steam. Tertiary base. H_2SO_4 and dilute KIO_3 form oxy-conessine $C_{60}H_{103}N_5O_6$ (?), a base which is coloured rose-red by conc. H_2SO_4 at 100° (W.).

Salts.—B'HCl aq: small very soluble needles. B'HNO_3: needles.—B'HCl.—$B'_2H_2Cl_2PtCl_4$ ½aq: very sparingly soluble yellowish-red needles.—B'$HClAuCl_3$ 1¼ aq: long yellow needles, v. sol. alcohol, nearly insol. water.—B'HCl,$AuCl_3$ 3½aq: golden-yellow needles.—B'$HClHgCl_2$: needles, sl. sol. water.

Picrate B'$C_6H_2(NO_2)_3OH$ aq: very slightly soluble glistening golden needles.

Methylo-iodide $C_{12}H_{20}NMeI$ 1½aq: tables. V. e. sol. hot water.

Ethylo-iodide $C_{12}H_{20}NEtI$ ½aq: glistening tables.

Methylo-hydroxide $C_{12}H_{20}NMe(OH)$: strongly alkaline base formed by the action of Ag_2O upon the iodide. It readily absorbs CO_2 forming the carbonate $(C_{12}H_{20}NMeO)_2CO$4aq, which crystallises in long needles. On heating to c. 150° it splits up into conessine and MeOH (Polstorff a. Schirmer, *B.* 19, 78).

CONGLUTIN *v.* Proteïds.

CONGO-RED *v.* *Amido-sulpho-naphthalene-azo-diphenyl-azo-naphthylamine sulphonic acid*, vol. i. p. 416.

CONHYDRÏN *v.* Coniine.

CONICEÏDINE *v.* Coniine.

CONICEÏNE *v.* Coniine.

CONIFERIN $C_{16}H_{22}O_8$. [185°]. S. (cold) ·51. $[\alpha]_D = -66{\cdot}9$ at 20° (*B.* 18, 1600).

Occurrence.—1. In the cambium of coniferous trees (Kubel, *J. pr.* 97, 243).—2. In small quantity in beet-root, and hence it gives rise to traces of vanillin sometimes found in beet-sugar (Lippmann, *B.* 16, 44).—3. In asparagus (*B.* 18, 3335).

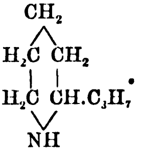
Preparation.—The juice of the cambial cells of fir trees is boiled, filtered, and evaporated to crystallisation.

Properties.—Satiny needles (containing 2aq). Efflorescent in dry air. V. sol. hot water, sl. sol. alcohol, insol. ether. Lævorotatory. Somewhat bitter. Its aqueous solution is not ppd. by metallic salts. Boiling dilute H_2SO_4 splits it up into glucose and a resin. Conc. H_2SO_4 gives a dark violet colour, and, on adding water, an indigo-blue pp. It is hydrolysed by emulsin into glucose and coniferyl alcohol. Phenol and H_2SO_4 give a blue colour, especially in sunlight. A dilute alcoholic solution of thymol and $KClO_3$ turns coniferin moistened with H_2SO_4 blue (Molisch, *C. C.* 1887, 366). Chromic mixture oxidises it to vanillin, giving the odour of vanilla (Tiemann). In weak alkaline solution sodium amalgam reduces it to eugenol (L. Chiozza, *C. C.* 1888, 443).

Tetra-acetyl derivative $C_{16}H_{18}Ac_4O_8$. [126°]. From coniferin and Ac_2O (Tiemann a. Nagai, *B.* 8, 1140). Crystalline. Insol. cold water, m. sol. cold alcohol and ether.

CONIFERYL ALCOHOL $C_{10}H_{12}O_3$ *i.e.* $C_6H_3(OH)(OMe)(C_3H_4OH)$. [4:3:1]. [74°]. Formed by subjecting an aqueous solution of coniferin to the action of emulsin at 25°: $C_{16}H_{22}O_8 + H_2O = C_6H_{12}O_6 + C_{10}H_{12}O_3$ (Tiemann a. Haarmann, *B.* 7, 611). Prisms. Sl. sol. hot water, m. sol. alcohol, v. sol. ether. Sol. alkalis and reppd. by acids in an amorphous condition, which softens at 160° and is v. sl. sol. alcohol and ether. This amorphous form is coloured red by conc. H_2SO_4, and afterwards dissolved with a red colour. Chromic acid mixture produces vanillin, which may be recognised by its characteristic odour; the other products of oxidation are HOAc and aldehyde. Potash-fusion gives protocatechuic acid. Sodium amalgam reduces it to eugenol $C_{10}H_{12}O_2$.

CONIINE $C_8H_{17}N$ *i.e.* $C_5H_{10}PrN$ or



Dextro-(α)-propyl-piperidine.

Mol. w. 127. (169°). S.G. $^{12\cdot5}$ ·846 (Petit, *B.* 10, 896); ·886 (Schorm). S. (cold) 1·11. S. (ether) 17. $[\alpha]_D = 13{\cdot}8$.

Occurrence.—In all parts of the hemlock (*Conium maculatum*) (Giesecke, Brande's *Ar. Ph.* 20, 97; Geiger, *Mag. Pharm.* 35, 72, 259; 36, 159; v. Planta a. Kekulé, *A.* 89, 129).

Synthesis.—(α)-Allyl-pyridine (from (α)-picoline and paraldehyde) on reduction with sodium and alcohol gives (α)-propyl-pyridine hexahydride; this (α)-propyl-piperidine is identical in all its properties with coniine, except that it is optically inactive, but by means of the acid tartrate it can be separated into a dextro- and a

lævo-base, the former of which is identical with natural coniine (Ladenburg, *B.* 19, 2579).

Formation. –1. By heating conhydrine with HI and phosphorus, and treating the resulting hydriodide of iodo-coniine with tin and HCl (Hofmann, *B.* 18, 5).—2. By reducing (α)-coniceine with HI and P (Hofmann).

Preparation. - 100 kilos. of hemlock seeds, after soaking in hot water till swollen, are mixed with a solution of 4 kilos. of Na_2CO_3 in 4 litres of water, and the mixture distilled with steam of about 3 atmospheres. The aqueous distillate is neutralised with HCl evaporated, NaOH added and extracted with ether. The residue after distilling off the ether is fractionated. Another method consists in extracting the ground seeds *in vacuo* with dilute acetic acid, evaporating the solution to a syrup *in vacuo*, adding magnesia, and extracting with ether (Schorm, *B.* 14, 1765; *cf.* Wertheim, *A.* 100, 328; 123, 157).

Properties.—Oil, smelling like mice. Is a violent paralytic poison which acts on the motor nerves (Hofmann, *B.* 14, 705; *cf.* Christison, *J. Ph.* 22, 413; *J. Chim. Med.* 12, 461; Kuhlmann, *N. Br. Arch.* 23, 38). For white mice the lethal dose is ·0758 g. per kilo., whilst ·0750 g. does not produce death (Ladenburg). Its aqueous solution becomes turbid on warming. Volatile with steam. Alkaline to moist test-papers. Coniine (100 pts.) dissolves water (25 to 30 pts.) and the solution when heated becomes turbid from separation of water. V. sol. alcohol, ether, chloroform, benzene, amyl alcohol, and acetone; sl. sol. CS_2. Coniine dissolves S but not P. Coniine gives a yellow pp. with phosphomolybdic acid, a cheesy pp. with potassio-mercuric iodide, and an orange pp. with potassio-bismuthic iodide. If coniine is dropped into a solution of alloxan, an intense-purple red colour is gradually developed, while white needles separate, which dissolve in cold KOHAq forming a purple solution (Schwarzenbach, *cf.* W. Blyth, *Poisons*, 1884, p. 251). Chloride of iodine gives a dark yellow pp. Coniine does not dissolve $CaCl_2$.

Estimation. Cripps, *Ph.* [3] 18, 511.

Reactions.—1. *Oxidises* readily in the air, becoming brown.—2. Boiling *chromic mixture* evolves *n*-butyric acid (Blyth; Grunzweig, *A.* 162, 193).—3. Alcoholic solution of *iodine* forms a dark brown pp. which afterwards disappears, the liquid becoming colourless.—4. *Bromine* forms a mass of needles [c. 100°]; if too much bromine is used a gummy mass is formed (Blyth).—5. *Chlorine* gas produces a turbidity in moist coniine. 6. Nitrous acid gas produces 'azoconhydrine' $C_8H_{16}N_2O$ (Wertheim, *A.* 123, 157).—7. By prolonged treatment with HI coniine is reduced to octane and NH_3 (Hofmann, *B.* 18, 5).—8. By distillation with *zinc-dust* it loses hydrogen and is converted into propyl-pyridine (conyrine) (Hofmann, *B.* 17, 825).—9. By the action of *bromine in alkaline solution* it gives a very unstable bromo- derivative which probably has the formula $C_8H_{16}NBr$. If this bromo- derivative is treated with H_2SO_4 it yields (α)-coniceine $C_8H_{15}N$ with splitting off of HBr. If however the elimination of HBr from the bromo- derivative is produced by treating it with alkalis (γ)-coniceine is obtained (Hofmann, *B.* 18, 109).—10. Reacts with *aldehydes* thus: $2C_8H_{16}NH + CH_3.CHO = (C_8H_{16}N)_2CH.CH_3 + H_2O$ &c. (Schiff, *B.* 6, 143).—11. *Chloroformic ether* forms $C_8H_{16}N.CO_2Et$ (245°). This is an oil, lighter than water, and very stable (Schotten, *B.* 15, 1917).—12. *Phenyl cyanate* forms the anilide of the same coniine ν-carboxylic acid $C_8H_{16}N.CO.NHPh$, which is v. sol. alcohol, ether, and benzene (Gebhardt, *B.* 17, 3041). 13. *Phenyl thiocarbimide* forms $C_8H_{16}N.CS.NHPh$ [88°] (G.).—14. *Phthalic anhydride* forms $CO_2H.C_6H_4.CO.N.C_8H_{16}$ [155°] the coniine salt of which when heated at 210° gives amorphous $C_6H_4{:}C_2O_2{:}(NC_8H_{16})_2$ (Piutti, *G.* 13, 558; *A.* 227, 181).

Salts.—$B'HCl$: [218°]. Colourless deliquescent laminæ. Dry HCl is said to colour dry coniine blue.—$B'_2H_2PtCl_6$: orange crystalline powder.—$B'HBr$: [100°] (Mourrut, *Ph.* [3] 7, 23). Trimetric needles; $a{:}b{:}c = {\cdot}8876{:}1{:}{\cdot}4218$. $B'HI$: flat monoclinic prisms; $a{:}b{:}c = 1{\cdot}2112{:}1{:}1{\cdot}1532$ (Schorm, *B.* 14, 1765).—$B'HI_3$: octahedra (Baur, *Ar. Ph.* [3] 5, 214).—Oxalate $B'_2H_2C_2O_4$: small crystals.—Tartrate $B'C_4H_6O_6$ 2aq: large trimetric crystals; $a{:}b{:}c = {\cdot}7766{:}1{:}{\cdot}5859$.

Combination.—$B'2HgCl_2$: lemon-yellow pp. (Blyth).—$B'H_2S$ (?). Unstable (Schmidt, *B.* 7, 1525).

Benzoyl derivative $C_8H_{16}NBz$. Thick oil. On oxidation with $KMnO_4$ it yields the benzoyl-derivative of homo-coniinic acid — $C_7H_{13}NBzCO_2H$ (Schotten a. Baum, *B.* 17, 2548).

Nitrosamine $C_8H_{16}N.NO$. *Azoconhydrine.* (150°–160°). From coniine by treatment with nitrous acid gas, followed by water (Wertheim, *A.* 123, 157; 130, 269). Yellow oil. V. sol. alcohol and ether. HCl passed into its ethereal solution reproduces coniine, giving off N and NO; zinc and HCl do the same.

Methyl-coniine $C_8H_{16}NMe$. From coniine and MeI. Formed also, together with C_2H_4 and H_2O, by distilling its ethylohydroxide (Kekulé a. Planta, *A.* 89, 143). Liquid.

Ethylo-hydroxide $C_8H_{16}NMeEtOH$. From the preceding by successive treatment with EtI and moist Ag_2O (K. a. P.). Strongly alkaline base.—$C_8H_{16}NMeEtI$: crystalline powder, not affected by aqueous KOH.—$C_8H_{16}NMeEtCl3HgCl_2$. $(C_8H_{16}NMeEtCl)_2PtCl_4$: yellow octahedra.—$C_8H_{16}NMeEtAuCl_4$.

Methylo-hydroxide $C_8H_{16}NMe_2OH$. From coniine by treatment with excess of MeI, the resulting iodide being decomposed by moist Ag_2O.

Di-methyl-coniine $(C_8H_{15}Me)NMe$. (182°). Prepared by the dry distillation of the methylo-hydroxide of methyl-coniine. Liquid.—$(B'HCl)_2PtCl_4$: sparingly soluble needles.

Methylo-iodide $C_8H_{15}MeNMe_2I$: crystalline solid.

Methylo-hydroxide $C_8H_{15}MeNMe_2OH$: on dry distillation it splits up into H_2O, CH_3OH, NMe_3, di-methyl-coniine, and conylene (C_8H_{14}) (Hofmann, *B.* 14, 708).

Ethyl-coniine $C_8H_{16}NEt$. From coniine and EtI, the resulting $C_8H_{16}NEtHI$ being decomposed by KOH (K. a. P.). Oil, smelling like mice.—$(C_8H_{16}NEt)_2H_2PtCl_6$: yellow crystalline powder.

Ethylo-iodide $C_8H_{16}NEt_2I$. Crystalline mass. Gives $(C_8H_{16}NEt_2Cl)_2PtCl_6$.

Oxy-ethyl coniine $C_8H_{16}N.CH_2.CH_2OH$. (241°). The hydrochloride is formed by the action of glycol chlorhydrin on coniine.

Benzoyl derivative $C_8H_{16}N.CH_2.CH_2.OBz$. From BzCl and the above.—$B'HI$: small pearly plates. $B'HCl$: very soluble crystals (Ladenburg, *B.* 14, 2109; 15, 1144).

Tri-bromo-oxy-coniine $C_8H_{11}Br_4ON$. Obtained as a by-product in the preparation of (γ)-coniceïne by treatment of coniine with bromine and alkali. Formed by the action of bromine and alkali upon (γ)-coniceine (Hofmann, *B.* 18, 121). Heavy oil. Very unstable. The free base quickly decomposes spontaneously into the hydrobromide and di-bromo-oxy-coniceine $2C_8H_{11}Br_4ON = C_8H_{11}Br_4ON,HBr + C_8H_{11}Br_2ON$. On reduction with tin and HCl it gives coniine and (γ)-coniceine.

Salts.—$B'HBr$: needles. $B'HNO_3$: very sparingly soluble. -$B'_2H_2Cl_2PtCl_4$: nearly insol. yellow crystalline pp.—$B'HClAuCl_3$: crystalline solid.

Di-methyl-oxy-coniine $C_8H_{15}Me_2ON$. (226°). Formed by the dry-distillation of the hydroxide of the ammonium-base $C_8H_{16}MeON,MeOH$, the iodide of which was obtained by digesting (γ)-coniceïne with methyl iodide and alcoholic NaOH (Hofmann, *B.* 18, 117). Colourless liquid. Sl. sol. water. Strongly alkaline. -$B'HCl,AuCl_3$: sparingly soluble crystals.

Homo-coniic acid $C_8H_{17}O_2N$ *i.e.* $CH_3.CH_2.CH_2.CH(NH_2).CH_2.CH_2.CH_2.CO_2H$ (?). [158°]. Obtained by saponification of the benzoyl derivative (Baum, *B.* 19, 502). White crystals; v. sol. water and alcohol. The aqueous solution reacts neutral. Optically inactive. Is not poisonous. It readily loses H_2O, and is converted into the inner-anhydride. When treated with nitrous acid it evolves nitrogen.

Benzoyl derivative $C_7H_{15}NBz.CO_2H$. [143°]. Formed by oxidation of benzoyl-coniine with $KMnO_4$ (Schotten a. Baum, *B.* 17, 2549). Needles or prisms; sol. alcohol, nearly insol. water and ether.—$A'Ag$: nearly insoluble white amorphous pp.—A'_2Cu: blue amorphous pp.; sl. sol. hot water, insol. alcohol.

Ethyl ether $C_7H_{15}NBz.CO_2Et$. [95°]. Long white flat prisms; v. sol. alcohol, ether, &c., nearly insol. water and petroleum-ether (Baum, *B.* 19, 500).

Inner anhydride $C_8H_{15}ON$. [85°]. Readily formed by splitting off H_2O from the acid by heating it to its melting-point, treating it with absolute alcohol, &c. (B.). White crystals. V. sol. water, alcohol, ether, and chloroform; m. sol. petroleum-ether. Sublimable. It is reconverted into the acid by boiling with baryta-water and ppg. the Ba with CO_2.

(α)-Coniceïne $C_8H_{15}N$. [c. −16°]. (158°). V.D. = 4·31 (obs.). S.G. ^{15} ·893.

Formation.—1. Together with (β)-coniceïne, by heating conhydrine $C_8H_{17}ON$ with P_2O_5.—2. Together with the (β)-coniceine, by heating conhydrine with HCl.—3. By the action of H_2SO_4 on the bromo- derivative $C_8H_{16}NBr$ obtained by treating coniine with bromine and NaOH. The yield is 40 p.c. of the coniine.—4. Together with (β)-coniceine, by heating iodo-coniine $C_8H_{16}IN$.

Properties.—Colourless liquid. Sl. sol. water. Its odour is extremely like that of coniine. Tertiary base of strongly alkaline reaction. Its physiological action resembles that of coniine, but it is about five or six times as poisonous. By HI and P it is reduced to coniine.

Salts.—$B'HCl$: six-sided tables.—$B'_2H_2Cl_2PtCl_4$: large yellow trimetric prisms.—$B'HClAuCl_3$: yellow needles.—**Picrate** $B'C_6H_2(NO_2)_3OH$ [225°]: yellow needles; sl. sol. cold alcohol, nearly insol. water.

Methylo-iodide $B'MeI$: crystalline solid; very sol. water and alcohol.—$(B'MeCl)_2PtCl_4$: yellow pp. (Hofmann, *B.* 18, 5).

(β)-Coniceïne $C_8H_{15}N$. [41°]. (168°). Formed together with (α)-coniceine (1) by heating conhydrine $C_8H_{17}ON$ with P_2O_5, (2) by heating conhydrine with fuming HCl, (3) by heating iodo-coniine $C_8H_{16}IN$ above 100°. Colourless needles. Very volatile. Coniine-like odour. Secondary base of strongly alkaline reaction. Weaker poison than the (α)-coniceine.

Salts.—$B'HCl$: colourless, very soluble prisms.—$B'HClAuCl_3$.

(γ)-Coniceïne $C_8H_{15}N$. (173°). Obtained by the action of aqueous alkali upon the bromo-derivative $C_8H_{16}NBr$ formed by treatment of coniine with bromine in alkaline solution; the yield is 30 p.c. of the coniine. Colourless liquid. Not solid at −50°. Volatile with steam. About 12 times more poisonous than coniine. Sl. sol. water. Strongly alkaline. Lighter than water. Secondary base. By further treatment with bromine and alkali it is converted into tri-bromo-oxy-coniine $C_8H_{11}Br_4ON$. By digesting with methyl-iodide and alcoholic NaOH it yields the methylo-iodide of **oxy-di-methylo-coniine** $C_8H_{15}Me_2ONMeI$.

Salts.—$B'_2H_2Cl_2PtCl_4$: large crystals; S (at 20°) 2·4.—$B'HClAuCl_3$: sparingly soluble crystals.—$B'_2H_2Cl_2SnCl_4$: large crystals, the most characteristic salt of the base.

Acetyl derivative $C_8H_{14}NAc$ (252°–255°); oil (Hofmann, *B.* 18, 111).

Oxy-coniceïne $C_8H_{15}ON$ (210°–220°). Formed by reduction of di-bromo-oxy-coniceïne with tin and HCl (Hofmann, *B.* 18, 125). Colourless fluid. Volatile with steam. By digestion with alcoholic KOH it loses H_2O and is converted into coniceïdine $C_{16}H_{26}N_2$.

Salts.—$B'HCl$: colourless needles.—$B'HClAuCl_3$: easily soluble thick needles. The stannic double chloride is sparingly soluble.

Di-bromo-oxy-coniceïne $C_8H_{13}Br_2ON$. Formed by spontaneous decomposition of tri-bromo-oxy-coniine, thus: $2C_8H_{11}Br_4ON = C_8H_{11}Br_4ON,HBr + C_8H_{13}Br_2ON$. Prepared by shaking the tri-bromo-oxy-coniine hydrobromide with aqueous NaOH and ether. By tin and HCl it is reduced to oxy-coniceine (Hofmann, *B.* 18, 124).

Coniceïdine $C_{16}H_{26}N_2$. [56°]. (above 300°). Colourless needles. Sol. alcohol and ether. Formed by elimination of H_2O from oxy-coniceïne by digesting it with alcoholic KOH.

Salts.—$B'HCl$: small sparingly soluble tables.—$B''H_2Cl_2PtCl_4$: nearly insoluble needles (Hofmann, *B.* 18, 126).

Conhydrine $C_8H_{17}NO$. *Oxy-coniine.* [121°]. (225°) at 720 mm. Accompanies coniine in hemlock seeds (Wertheim, *Sitz. W.* 47 [2] 299). Glittering plates (from ether). M. sol. water, v. sol.

alcohol and ether. Alkaline. Does not react with nitrous acid. Is a weak narcotic poison.

Reactions.—1. By the action of P_2O_5 it is not converted, as Wertheim (*A.* 127, 75) supposed, into coniine, but into a mixture of (α)- and (β)-coniceine $C_8H_{15}N$. These products are also formed by heating conhydrine with strong HCl (Hofmann, *B.* 18, 5).—2. By heating with HI and P it is converted into an iodo-coniine $C_8H_{16}IN$, which on heating above 100° is converted into the hydroiodides of (α)- and (β)-coniceine, and is reduced by tin and HCl to coniine.—3. PBr_3 converts it into a bromo-coniine $C_8H_{16}BrN$.

Salt. -$B'_2H_2PtCl_6$: red crystals. The sulphate is also crystalline.

Ethyl-conhydrine $C_8H_{16}EtNO$. Formed by the action of KOH on the crystalline compound of conhydrine with EtI. Oil.

Ethylo-iodide $C_8H_{16}EtNOEtI$. Trimetric crystals; $a:b:c$ = ·8823.1: ·105 (Zepharovich, *Sitz. W.* 47 [1] 275). Converted by Ag_2O into a caustic ethylo-hydroxide, whence HCl and $PtCl_4$ give $(C_8H_{16}EtNOEtCl)_2PtCl_4$: dimetric crystals; $a:c$ = 1: ·870.

Paraconiceine $C_8H_{15}N$. *Paraconiine.* Mol. w. 125. (169°). S.G. ^{0} ·913; ^{99} ·842.

Formation.—1. By heating butyric aldehyde with alcoholic NH_3 and distilling the resulting dibutyraldine (Schiff, *A.* 157, 352; 166, 88; *B.* 5, 12).—2. From butylidene chloride $CH_3.CH_2.CH_2.CHCl_2$ (or bromide) and alcoholic NH_3 at 180° (Michael a. Gundelach, *Am.* 2, 172; *B.* 14, 2105).

Properties.—Yellow liquid, smelling like coniine. V. sol. alcohol and ether; sl. sol. water. The aqueous solution becomes turbid when warmed. Inactive. As poisonous as coniine. Chlorine water produces in the aqueous solution a white pp., sol. HCl. The hydrochloride, when evaporated, becomes violet. Iodine dissolved in KI gives a brown pp. Is a tertiary base. $B'_2H_2PtCl_6$: orange crystals.

'Paradiconiine' $C_{16}H_{27}N$. (210°). S.G. ^{15} ·915. Formed, together with paraconiceine, by the prolonged action of alcoholic NH_3 on butyric aldehyde. Its salts are amorphous.

CONIMENE $C_{15}H_{24}$. (264°). An essential oil obtained by steam-distillation from conima or incense-resin (called also Gum Hyawa), the produce of *Icica heptaphylla* (Stenhouse a. Groves, *C. J.* 29, 175).

CONQUINAMINE *v.* Cinchona bases.

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CONSTITUTION, CHEMICAL (*cf.* Composition, chemical).—The conception of chemical constitution is a development of that of chemical combination. All our present notions on the subject of constitution are essentially molecular and atomic. We cannot, indeed, express our conceptions of chemical constitution without using the language of the molecular theory. The chemical molecule is regarded as a definite structure built up of atoms, or groups of atoms, which are related to one another in a definite, although as yet unknown, way. The properties of the molecule are regarded as conditioned by the nature and number of the atoms, and also by the relations between the atoms, which form the molecule. Our only method of expressing the relations which undoubtedly exist between the parts of molecules is based on supposing these relations to be essentially space-relations. We try to picture the molecule as a configuration of parts, each of which bears a definite space-relation to each other, while all are capable of performing regulated motions without the disruption of the molecule.

This conception of the molecule as a structure is developed in the hypothesis of valency, and attempts are made to give consistent representations of it, with the help of certain conventions, in constitutional or structural formulæ (*v.* Equivalency; Formulæ; Isomerism).

M. M. P. M.

CONTACT ACTION *v.* Chemical change.

CONVALLAMARIN $C_{23}H_{44}O_{12}$. Occurs, together with convallarin, in the lily of the valley (*Convallaria majalis*) from which plant it may be extracted by alcohol (Walz, *N. Jahrb. Pharm.* 1858, 10, 115; Langelbert, *J. Ph.* [5] 10, 26; *C. J.* 48, 271). Powder, with bitter taste, v. sol. water and alcohol, v. sl. sol. ether. Decomposed by boiling dilute H_2SO_4 into glucose and convallamaretin, which separates in crystalline spangles, and becomes resinous in boiling water.

Convallarin. Rectangular columns. Insol. water and ether, v. sol. ether. Resolved by boiling dilute acids into glucose and convallarin.

CONVICIN *v.* Vicin.

CONVOLVULIN $C_{31}H_{50}O_{16}$. [150°]. Occurs in tuberose or officinal jalap root (from *Convolvulus Schiedanus*), and may be extracted from jalap resin by washing with ether, then exhausting with alcohol, and evaporating the alcoholic extract (Mayer, *A.* 95, 161; A. F. Stevenson, *Ph.* [3] 10, 644). A hard resin. Odourless, tasteless. Sol. chloroform, and hydro-chloric acid; insol. water, ether, light petroleum, CS_2, benzene, and oil of turpentine. After being taken internally it is not secreted unaltered (Dragendorff, *C. C.* 1886, 589). Dissolves in H_2SO_4 to a bright red colour. Potassium chromate, permanganate, nitrate, or chlorate give an odour of rancid butter and an olive green colour. Conc. HNO_3 gives oxalic acid and ipomic acid $C_{10}H_{18}O_4$.

Convolvulic acid $C_{31}H_{52}O_{17}$ (?) [100°–120°]. Formed by boiling convolvulin with baryta-water (Kayser, *A.* 51, 81; Mayer, *A.* 83, 126; 95, 162). White hygroscopic substance; sol. water and alcohol, insol. ether.

Salts.—$KA'\frac{1}{2}aq$: [100°–110°]; amorphous.—BaA'_2.—PbA'_2.

Convolvulinolic acid $C_{26}H_{48}O_6aq$. [39°]. Formed, together with glucose, by the action of emulsin or of dilute acids on convolvulic acid. Minute needles: v. sl. sol. water, v. e. sol. alcohol, m. sol. ether. Tastes bitter. Conc. H_2SO_4 turns it red. Conc. HNO_3 gives oxalic and ipomic acids. The same body, or an isomeride, is formed by fusing convolvulin or convolvulic acid with moist NaOH. It forms salts: BaA'_2aq (at 100°).—PbA'_2.—$CuA'_2\frac{1}{2}aq$ (at 100°).

CONYLENE *v.* Octinene.

CONYLENE BROMIDE *v.* Di-bromo-octylene.

CONYLENE GLYCOL *v.* Di-oxy-octylene.

CONYRINE is (α)-Propyl-pyridine (*q. v.*).

COPAIBA BALSAM. Exudes from incisions in the stems of various species of *Copaifera*. Diuretic.

It contains a lævorotatory terpene (**Copaiba oil**) $C_{20}H_{32}$ (250° 260°); S.G. ·9; V D 9·5. The terpene from ordinary copaiba balsam yields a crystalline hydrochloride $C_{20}H_{32}4HCl$ [77°], but those from Maracaibo balsam do not (Bonastre, *J. Ph.* 11, 529; Ader, *J. Ph.* 15, 95; Gerber, Brande's *Arch.* 30, 157; Blanchet, *A.* 7, 156; Souberran a. Capitaine, *J. Ph.* 26, 70; *A* 34, 321; Posselt, *A.* 69, 67, Lowe, *Ph.* 11, 65; Strauss, *A.* 148, 151). The terpene from Maracaibo balsam yields terephthalic acid on oxidation (Brix, *M.* 2, 507). Moist copaiba oil distilled over sodium gives a dark blue hydrate $C_{20}H_{32}$ ½aq (252° 260°). The different varieties of copaiba balsam also contain resins and resinous acids (Stoltze, *Jahrb f. Pharm.* 27, 179; Oberdorfer, *Ar. Ph.* [2] 14, 172; Ulek, *Ar. Ph.* 122, 14; Stockhardt, *Ar. Ph.* 38, 12, Procter, *Ph.* 10, 603; Roussin, *J. Ph.* [4] 1, 321; Schweizer, *P.* 17, 784; 21, 172; Rose, *P.* 33, 83; Hess, *A.* 29, 140; Fehling, *A.* 40, 110; Wayne, *Am. Journ. Pharm.* [4] 3, 326; Siebold, *Ph.* [3] 8, 250; Bowman, *Ph.* [3] 8, 330; Martin a. Vigne, *J. Ph.* 1842, 52). On oxidation with $K_2Cr_2O_7$ and H_2SO_4 copaiba balsam yields *u*-di-methyl-succinic acid [140°] (Levy, *B.* 18, 3206).

Copaivic acid $C_{20}H_{32}O_2$ (?) Extracted by alkalis from copaiba balsam (Rose, *A.* 13, 177; 40, 310; Fluckiger, *J. pr.* 101, 235; Rush, *Ph.* [3] 10, 5). Crystalline. CaA'_2.—PbA'_2. AgA'.

Metacopaivic acid $C_{22}H_{34}O_4$. [206°]. Extracted by alkalis from Maracaibo balsam obtained from Columbia (Strauss, *A.* 148, 153). Plates. Insol. water, v. sol. alcohol and ether.—CuA''aq. Ag_2A''aq.

Oxycopaivic acid $C_{20}H_{28}O_3$. [c. 120°]. Found in a balsam from Para (Fehling, *A.* 40, 110). Crystals. Forms an amorphous hydrate $C_{20}H_{30}O_4$. PbA'_2.—AgA'.

COPAL. This name is given to a variety of resins which exude from different trees, *e.g.* *Rhus copallina*, *Elæocarpus copalifer*, *Hymenæa verrucosa*, *Dammara australis*. They contain many resins, and often yield terpenes on distillation (Filhol, *A.* 44, 323; Thomson, *A.* 47, 351; Schibler, *A.* 113, 339; Unverdorben, *B. J.* 11, 265; Violette, *C. R.* 63, 161; Muir, *C. J.* 27, 733; Rennie, *C. J.* 39, 240). A similar substance (copalm) is found fossilised at Highgate (Johnston, *P. M.* [3] 14, 87).

COPELLIDINE *v.* TRI-METHYL-PYRIDINE HEXAHYDRIDE.

COPPER GROUP OF ELEMENTS. COPPER, SILVER, GOLD. These metals occur native; they have been known and used from very early times. They show a general resemblance to each other in their physical and chemical properties, but there are differences between them. The table in the next column presents some of their properties.

The three metals are hard, lustrous, malleable, tenacious, and ductile; they are good conductors of electricity; they crystallise in forms belonging to the regular system. Cu is oxidised by treating in air; Ag combines very slowly with O at extremely high temperatures; Au does not directly combine with O. Cu and Ag interact with acid to form salts; Au is acted on by *aqua regia*, but not by HClAq or HNO_3 separately. Cu decomposes steam at a red heat; Ag and Au are without action on steam.

	Copper	Silver	Gold
Atomic weight .	63 2	107·66	197
Molecular weights are unknown.			
Melting-point . .	c. 1100°	c. 1000°	c. 1200°
Specific gravity (approximate)	8·8	10 5	19 5
Atomic weight / *Specific gravity* .	7·2	10 3	10 1
Specific heat . .	·095	·057	·0324
Heats of formation of various compounds (Thomsen).			
[M²,Cl²] . . .	65,750	58,760	11,620
[M²,O] . . .	40,810	5,900	
[M²,S] . . .	20,270	5,340	
Heats of neutralisation of oxides (Thomsen).			
[M²O,2HClAq] .	19,300	12,580	[AuO³H³,3HClAq] =18,440

General formulæ and character of compounds.—*Oxides*, MO and M_2O, also Au_2O_3. *Sulphides*, MS (except Ag), M_2S. *Haloid compounds*, MX_2 (except Ag), MX or M_2X_2, AuX_3. *Salts*, Cu_2X, Ag_2X, and a few Au_2X; CuX; a few Au_23X; (X = SO_4, $2NO_3$, CO_3, $\frac{2}{3}PO_4$, S_2O_3, &c). The oxides Cu_2O and Au_2O are produced by reducing cupric and auric salts, *e.g.* $CuSO_4$Aq and $AuCl_3$Aq, in presence of an alkali; Ag_2O is obtained by adding alkali to an argentous salt, *e.g.* $AgNO_3$Aq. Addition of alkali to a cupric salt, *e.g.* $CuSO_4$Aq, ppts. $CuO.H_2O$, which loses water on heating to dull redness; addition of alkali to an auric salt, *e.g.* $AuCl_3$Aq, ppts. $Au_2O_3.3H_2O$, which loses water at 100°, and at a higher temperature becomes AuO; argentic oxide AgO is formed by the action of ozone on Ag_2O. Of the oxides of Cu, CuO is the more stable; it dissolves in acids and forms a large series of well-marked salts; Cu_2O forms a few salts by directly interacting with acids, but generally it reacts to form salts of CuO with separation of Cu. Of the oxides of Ag, Ag_2O is much the more stable; it reacts with acids to form argentous salts; AgO acts towards acids as a basic peroxide, forming argentous salts and evolving O. None of the oxides of Au is stable; a few salts corresponding to each are known, *e.g.* $Au_2S_2O_3$ derived from Au_2O, $AuSO_4$ from AuO, and $AuCl_3$ from Au_2O_3. The oxides of Cu and Ag are distinctly basic; moist Ag_2O acts like a weak alkali, although a hydroxide has not been certainly isolated. Au_2O and AuO are feebly basic; Au_2O_3 is also feebly basic, but it likewise dissolves in KOHAq to produce a salt, $KAuO_2$, in which Au forms part of the negative radicle.

The sulphides Cu_2S and Au_2S are produced by the combined action of H_2S and reducing agents on cupric and auric salts; *e.g.* a cupric salt heated in H_2S and then in H gives Cu_2S; $AuCl_3$ dissolved in KCNAq and ppd. by H_2S gives Au_2S. Argentous salts give Ag_2S on addition of H_2S. The sulphides CuS and AuS are formed by reactions between H_2S and cupric or auric salts. Both sulphides of Cu, and sulphide of Ag, are stable; Cu_2S being the more stable of the Cu sulphides. These sulphides are basic, forming some compounds with the sulphides of less positive elements, *e.g.* $Cu_2S.Sb_2S_3$; Cu_2S also forms some double compounds in which it appears to be negative to the other constituent, *e.g.* $K_2S.3Cu_2S.2CuS$. Au_2S when freshly ppd. dissolves in water; both this sulphide and AuS dissolve in alkali sulphides to form sulpho-salts, *e.g.* NaAuS, $KAuS_2$.

The salts of Cu belong to two series; *e.g.* Cu_2Cl_2 representative of cuprous salts, and $CuSO_4$ representative of cupric salts; the cupric salts are the more stable. Silver forms but one series of salts, the argentous salts, *e.g.* $AgNO_3$, Ag_2SO_4. Few gold salts are known; $Au_2S_2O_3$ is a representative of the aurous salts, $AuSO_4$ represents the auro-auric salts, and $AuCl_3$ belongs to the auric series. Auric chloride and bromide $AuCl_3$ and $AuBr_3$ combine with HCl and HBr respectively, forming the monobasic acids $HAuCl_4$ and $HAuBr_4$. Gold is distinctly the most negative of the three elements Cu, Ag, Au; the non-metallic character of Au is shown in the formation of aurates, *e.g.* $KAuO_2$, derived from Au_2O_3, of sulpho-aurates, *e.g.* NaAuS and $KAuS_2$, derived from AuS, of the acids $HAuCl_4$ and $HAuBr_4$, and in the instability of the salts of Au. Silver is distinctly metallic in all its chemical relations. Cu is also metallic, but the formation of such compounds as $K_2S.3Cu_2S.2CuS$ shows a tendency of Cu to react as a feebly non-metallic element.

The position of the elements Cu, Ag, Au in the scheme of classification based on the periodic law is peculiar (*v.* Classification, p. 204). These elements are placed in Group I.; this group comprises Li, Na, K, Rb, and Cs, which are the most positive, and chemically the most metallic, of all the elements; but Cu finds a place in the *long period* containing the metals Fe, Ni, and Co; Ag comes in the *long period* which contains Rh, Ru, and Pd; and Au follows Os, Ir, and Pt. The three sections of Group VIII., viz. (1) Fe, Ni, Co, (2) Rh, Ru, Pd, (3) Os, Ir, Pt, appear to impress their own properties on the elements immediately preceding and succeeding them. Cu, Ag, and Au exhibit analogies at once with the other members of the group to which they belong, and with those metals of Group VIII. which form part of the *long periods* including Cu, Ag, and Au respectively. The analogies with the metals of Group VIII. are shown in the physical properties of Cu, Ag, and Au, and also to some extent in their general chemical characters. The analogies between the alkali metals and the elements of the Cu group are shown in the composition of the alkali salts and the cuprous salts, the argentous salts, and the few aurous salts which have been isolated; also in the basic character of cuprous, argentous, and aurous oxides. The existence of AgO and CuO_2, and the fact that these behave as peroxides, establishes an analogy between Cu and Ag on one side, and Na or K on the other; Ag also forms an alum, $Ag_2SO_4.Al_2(SO_4)_3.24H_2O$; moist Ag_2O reacts as a weak alkali; the non-existence of any salts of Ag except those of the type AgX ($X = \frac{SO_4}{2} = NO_3$, &c.) establishes another resemblance between Ag and the alkali metals. It should be noted here that the molecular formula of cuprous chloride is Cu_2Cl_2, while that of silver chloride is AgCl; in this point Ag resembles the alkali metals, as the molecular formulæ KCl and CsCl have been established. Au differs more than either Cu or Ag from the alkali metals; this difference is emphasised in the acidic characters of Au_2O_3, Au_2S, and AuS, in the formation of $HAuCl_4$, &c., and in the great instability of the salts of Au; on the other hand, the solubility in water of Au_2O and Au_2S suggests the solubility in water of the oxides and sulphides of the alkali metals. The methods of formation of Au_2O and Au_2S suggest the processes by which Cu_2O and Cu_2S are formed. (For more details about the metals of the copper group, *v.* Copper, Silver, Gold; *v.* also Noble metals.) M. M. P. M.

COPPER. Cu. At. w. 63·2. Mol. w. unknown (c. 1100°; for various determinations *v.* Carnelley's *Melting and Boiling Points*). S.G. varies from 8·36 for finely divided Cu to 8·95 for hammered Cu (*v.* Playfair a. Joule, *C. S. Mem.* 3, 57; Dick, *P. M.* [4] 11, 409; Baudrimont, *J. pr.* 7, 287; Hampe, *C. C.* 6, 379; Marchand a. Scheerer, *J. pr.* 27, 193, &c.). S.H. (15°–100°) ·0933; (16°–172°) ·0948; (17°–247°) ·0968 (Bède, *Mem. B.* 27 [1855–56]. C.E. (linear 0°–100°) ·00001666 (Matthiessen, *Pr.* 15, 220). C.E. (cubical) $V_t = V_o (1 + \cdot00001443t + \cdot00000000555t^2)$ (Matthiessen, *l.c.*). T.C. (Ag = 100) 73·6 (Wiedemann a. Franz, *P. M.* [4] 7, 33). E.C. at c. 19° (Ag wire = 100), 93 (Matthiessen, *Tr.* 1860; *Pr.* 11, 126). E.C. at 0° (Hg at 0° = 100) c. 52–54 (Siemens, *P. M.* [4] 21, 24). E.C. is much decreased by small quantities of P, As, Zn, Fe, Sn, &c. (*v.* Matthiessen, *l.c.*). Emission-spectrum characterised by lines in the green 5217, 5153, and 5105 (Thalén) Hartley (*Tr.* 1881. 105) gives the following as prominent lines of high refrangibility: 3273·2 3246·9, 2544·6, 2370·1, 2248·2, 2247·7, 2244, 2213·5. Crystallises in regular octahedra. S.V.S. c. 7·1.

Occurrence.—Very abundantly; as metal, oxide, sulphide, chloride, arsenate, carbonate, phosphate, sulphate, silicate, and vanadate. Small quantities of salts of Cu are found in seaweed (Malaguti, *A. Ch.* [3] 28, 129); in sea-water (Dieulafait, *A. Ch.* [5], 18, 349); in the blood of various animals (*v.* Harless, *Chem. Gazette*, 1848. 214; Genth, *P.* 95, 60; *J.* 1848. 871, 874; 1849. 530; Ulex, *J. pr.* 94, 376; Wicke, *W. J.* 1866. 73); in flour, eggs, &c. (Odling a. Dupré, *Guy's Hospital Reports*, October 1858); in all plants that live on primary rocks or on soil derived from these rocks (Dieulafait, *A. Ch.* [5] 19, 550). In many mineral waters. Copper has been known and used for making tools from very early times.

Formation.—1. From native oxides and carbonates by melting with silica in presence of lime and charcoal; silicate of calcium is formed and the charcoal reduces the oxide of copper. — 2. From native sulphides, and sulphides of Cu with Fe, &c., by roasting and then melting; CuO is first formed, and then reacts with FeS in the ores to form CuS and Fe_2O_3, the greater part of the iron passes into the slag; by repeating this process approximately pure CuS is obtained; this is roasted so as to convert a part of it into CuO, the mixture of CuO and CuS is melted in closed apparatus when SO_2 and Cu are produced ($2CuO + CuS = 3Cu + SO_2$); the impure copper is refined by *poling*, a process consisting in stirring the melted metal, covered with a layer of anthracite, with a green pole of birch or oak, the heated wood evolves reducing gases (CO, H_2O, hydrocarbons).—3. From oxide, or from roasted native sulphides, by treatment with heated conc. NaClAq whereby $CuCl_2$ is formed and dissolved, followed by ppn. by means of scrap iron.—4. From oxide, or from roasted native sulphides, by treatment with hot NaClAq and $FeSO_4$Aq mixed with $CaCl_2$ and subsequent ppn. by scrap iron; the chief reaction is $3CuO + 2FeCl_2Aq = Fe_2O_3 + Cu_2Cl_2Aq + CuCl_2Aq$. 5. By electrolysis of solution of Cu salts.

Preparation.—1. Commercial copper is dissolved in fairly conc. H_2SO_4Aq; $PbSO_4$ is ppd. by diluting largely with water; the liquid is filtered and poured on to Zn or Fe (sifted Zn powder is best), and digested until nearly but not quite colourless; the pp. is freed from Zn or Fe by treatment with warm dilute HClAq; it is then washed, dried, and fused under borax; or the pp. of Cu after digestion with acid is washed, dried quickly at 75°, and heated in a stream of H (Bottger, *A.* 39, 172). [For impurities in commercial copper *v.* Abel a. Field, *C. J.* 14, 280.] 2. $CuSO_4$Aq is mixed with $KC_2H_3O_2$Aq, and H_3PO_2Aq is added; Cu ppts. quickly (Wohler, *A.* 79, 128).—3. Commercial copper is dissolved in equal parts of H_2SO_4 and water; the solution is boiled with a little HNO_3 (to oxidise Fe salts) and crystallised, the crystals are recrystallised from water, dissolved and electrolysed (Millon a. Commaille, *C. R.* 56, 1249). 4. Hampe (*Fr.* 1874. 352) adds KOHAq to $CuSO_4$Aq until a pp. of basic salt is formed (this pp. contains any Bi which might have been present in the $CuSO_4$); the filtered solution is evaporated and crystallised; the crystals are dissolved in the smallest possible quantity of water; 20 cc. conc. HNO_3Aq are added to every 500 cc. solution; an electric current is passed through this liquid using cone-shaped Pt electrodes, the current being stopped before the whole of the Cu is ppd., whereby Fe, Zn, and other metals remain in solution; the ppd. Cu is washed and dissolved in pure HNO_3Aq, the solution is evaporated to dryness, and the $Cu(NO_3)_2$ obtained is decomposed by heating; the CuO is reduced by heating in pure H. The Cu thus obtained is dissolved in H_2SO_4Aq; crystals of $CuSO_4$ are obtained, and the foregoing process of electrolysis is repeated. The metal obtained by the second electrolysis is boiled in water, to remove traces of undecomposed $CuSO_4$. The Cu thus obtained is heated to a very high temperature in a porcelain tube in a current of pure CO_2 (about 50 grams Cu at a time) until melted. H is then passed over the molten metal for a time, and finally it is allowed to cool in CO_2.—5. Finely divided Cu may be obtained (*a*) by reducing CuO in a stream of H; (*b*) by strongly heating a mixture of 5 parts Cu_2Cl_2 with 6 parts dry Na_2CO_3, and some NH_4Cl, and washing the product (Liebig a. Wohler, *P.* 21, 582); (*c*) by digesting $CuSO_4$Aq with sifted zinc powder, pouring off the liquid before quite colourless, washing the residue with dilute HClAq, pressing between paper, and drying at about 75°.

Properties.—A reddish-yellow solid. The red colour of ordinary Cu is due to a film of Cu_2O. Crystallises from molten state, or by slow electrolytic deposition, or by ppn. by means of P, in cubes and octahedra belonging to the regular system. Melts at high temperature, about 1100°; expands on solidifying; very ductile, malleable, hard, and elastic; fairly tenacious; very good conductor of heat and electricity; may be highly polished; sonorous. Copper melted in air assumes a vesicular structure on cooling owing to escape of bubbles of gas, either CO formed when the Cu is melted under charcoal, or SO_2 formed by action of traces of S in the Cu on traces of CuO present (Dick, *P. M.* [4] 11, 409; Matthiessen a. Russell, *P. M.* [4] 23, 81). Finely divided Cu may readily be hammered and pressed into masses. Cu is slightly volatile when very strongly heated (Riemsdyk, *C. N.* 20, 32); in the O-H flame it boils and partially volatilises; Despretz (*C. R.* 48, 362) volatilised Cu in a H stream by passing a current through it from 600 Bunsen-cells. Molten Cu absorbs various gases (Hampe, *Zeitschr. f. d. preuss. Berg-Hutten und Salinen Wesen*, 1874 a. 1875; Graham, *P. M.* [4] 32, 503; Lucas, *A. Ch.* 12, 402; Marchand a. Scheerer, *J. pr.* 27, 195; Dick, *P. M.* [4] 11, 409; Matthiessen a. Russell, *P. M.* [4] 23, 81; Lenz, *J. pr.* 108, 438). H is absorbed in considerable quantity (finely divided Cu absorbs ·6 vols. of H, Graham); the whole of the H is not given out on cooling, or on heating to 160° (Lietzenmayer, *B.* 11, 306); but if the Cu is heated to 250° it is slightly oxidised, and if it is then heated to redness in a nearly closed tube a little H_2O is formed, and the CuO is reduced (L., *l.c.*). Cu prepared by reducing CuO in H retains a little H, which may be removed by the method described; or by heating in a stream of formic acid vapour (Wegl, *B.* 15, 1139). SO_2 and CO are also absorbed by molten Cu; CO_2 and N are not absorbed. Cu in masses is unchanged in dry air; when gently heated it is superficially oxidised to Cu_2O, at a higher temperature Cu_2O and CuO are formed; finely divided Cu burns to CuO in air considerably under a red heat. In moist air containing CO_2, Cu becomes covered with a film of greenish basic carbonate; after a considerable time the interior of such Cu contains crystals of Cu_2O (*D. P. J.* 206, 200). Finely divided Cu, obtained by reducing CuO under red heat, is changed by ordinary air to Cu_2O. Cu in mass decomposes H_2O at a full red heat, and then only slowly. Cu is slowly acted on by many dilute organic acids in the air; eatables should not, therefore, be allowed to remain in Cu vessels exposed to air, although they may be boiled with water in such vessels, as then the escaping steam removes the air. Cu is slightly dissolved by HClAq or H_2SO_4Aq in presence of air; conc. hot H_2SO_4 forms $CuSO_4$ and CuS with evolution of SO_2; conc. hot HIAq forms Cu_2I_2 and H; HNO_3Aq readily dissolves the metal with evolution of N oxides; SO_2Aq slowly forms $CuSO_3$ and H_2SO_4Aq. NH_3Aq, in presence of O, acts on Cu, forming Cu-NH_4 nitrate; heated in NH_3, Cu nitride is formed. NH_4 salts, and some other metallic salts, in solution dissolve appreciable quantities of Cu. Cu combines directly with Cl, Br, S, P, Si, As, Sb, and many metals (*v.* COPPER, ALLOYS OF).

The atomic weight of Cu has been determined (1) by reducing CuO in H (Berzelius, *P.* 8, 182; Erdmann a. Marchand, *J. pr.* 31, 391; Millon a. Commaille, *C. R.* 57, 147; Hampe, *Fr.* 13, 354); (2) by electrolysing $CuSO_4$Aq and weighing the Cu (Hampe, *Fr.* 13, 367; Shaw, *P. M.* [5] 23, 138); (3) by reducing $AgNO_3$Aq by pure Cu and weighing the Ag (Richards, *P. Am. A.* 22; 23, 177). The number 63·2 is confirmed by the S.H. of Cu, and by comparison of the crystalline forms of Cu compounds with some ferrous compounds, and also with compounds of Co and Ni, and with some compounds of Ag.

Copper is distinctly a metallic element; it forms salts by replacing the H of most acids; most of these salts belong to the series CuX_2 where $X = Cl, NO_3, \frac{SO_4}{2}$, &c.; but several *cuprous* salts, Cu_2X_2, are also known. There are indications of the existence of compounds of Cu with strongly positive metals and O, in which the Cu forms part of the negative radicle of the salts, but such salts have not been isolated (*v.* Copper, oxides of). Copper is analogous in its chemical relations on one hand to Ag, and on the other to Fe, Ni, and Co; it also shows similarities with Au and with the alkali metals. In the periodic classification of the elements Cu is generally placed both in Group VIII., which comprises Fe, Ni, Co, and the Pt metals, and also in Group I., which includes H, the alkali metals, Ag, and Au (*v.* Copper group of elements). The valency of the atom of Cu has not been determined with certainty; the only compound whose molecular weight in the gaseous state has been determined is Cu_2Cl_2, the atom of Cu is most probably divalent in this molecule.

Allotropic form of copper. Schützenberger (*C. R.* 86, 1265) described a bronze-coloured solid, obtained by electrolysing a solution of Cu acetate containing some basic acetate (produced by boiling); the negative electrode consisted of a plate of Pt, and the positive of a somewhat larger Cu plate; 2 Bunsen- or 3 Daniell-cells were used; the electrodes were placed 3 or 4 centims. apart. The bronze-coloured body was deposited on the face of the Pt electrode turned towards the Cu plate. The deposit was lustrous; very brittle; S.G. c. 8 to 8·2; it contained 5 to 10 p.c. CuO; it was oxidised readily in moist air; cold HNO_3Aq (10 p.c.) dissolved it readily with evolution of nearly pure N_2O. This substance was changed to ordinary Cu by heat. No H was evolved by heating to 100° in CO_2. Wiedemann (*W.* 6, 81) says that the substance obtained by electrolysing Cu acetate as described is ordinary Cu containing CuO sometimes amounting to 35 p.c.; Schutzenberger (*Bl.* [2] 31, 291) asserts that his *allotropic copper* is changed to ordinary copper without change of mass (*v.* also Mackintosh, *C. N.* 44, 279).

Reactions.—1. Cu decomposes *water* slowly at a full red heat (Regnault, *A. Ch.* 62, 364).—2. In dry *air* Cu is unchanged; but in ordinary moist air it becomes covered with a film of a basic carbonate (*D. P. J.* 206, 200), and crystals of Cu_2O are formed in the interior of the mass.—3. Heated in *oxygen* CuO is formed; very finely divided Cu is said to form Cu_2O in oxygen without heating.—4. Not acted on by *weak acids in absence of air*, but slowly dissolved by dilute HClAq, &c., in presence of air. Thomsen gives these thermal data (*Th.* 3, 320):—$[Cu, O^2, SO^4] = 111,490$; $[Cu, O^2, 2NO^2, 6H^2O] = 96,950$; $[Cu, O, H^2SO^4Aq] = 55,960$; $[Cu, O, 2HNO^3Aq] = 52,410$.—5. In very conc. *nitric acid* Cu is *passive*, because of formation of layer either of NO or CuO (*cf. Passivity of Iron*, under Iron). Dissolves rapidly in less conc. nitric acid giving off NO and N_2O.—6. Conc. *hydrochloric acid* in presence of air dissolves finely divided Cu, forming Cu_2Cl_2 and evolving H (Odling, *C. J.* 9, 291); less conc. HClAq slowly dissolves Cu when heated with it in presence of air. 7. Dilute *sulphuric acid* in presence of oxygen slowly dissolves Cu (forming H_2O_2 according to Traube, *B.* 18, 1887). Conc. H_2SO_4 acts on Cu even at 20°, forming Cu_2S, and $CuSO_4$; at higher temperatures SO_2 is evolved, until at 270° the action is represented by the equation $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$ (Pickering, *C. J.* [2] 18, 112).—8. *Sulphurous acid* slowly acts, forming sulphite and H_2SO_2Aq; if large excess of H_2SO_3Aq is used, CuS is formed along with S (Causse, *Bl.* [2] 45, 3).—9. Conc. hydriodic acid attacks Cu forming Cu_2I_2 and H.—10. Aqueous solutions of many *metallic salts* slowly dissolve Cu; chlorides and nitrates, especially of ammonium, are the most active (*v.* Pattison Muir, *C. N.* 34, 223, 234; Carnelley, *C. J.* [2] 15, 1). According to Traube (*B.* 18, 1887) Cu dissolves in $(NH_4)_2CO_3Aq$ with production of H_2O_2Aq.—11. *Ammonia solution* slowly dissolves Cu with previous formation of CuO; Schonbein (*B. B.* 1856. 580) says that $Cu-NH_4$ nitrite is produced. Heated in *ammonia* to full redness, Cu becomes brittle and now contains N, a nitride is probably formed (Warren, *C. N.* 55, 155).—12. *Sulphuretted hydrogen* forms CuS.—13. Many *fatty oils, e.g.* olive, rape, linseed, &c., dissolve considerable quantities of Cu (Thomson, *C. N.* 34, 176, 200, 213).

Combinations.—Copper combines directly with the following non-metallic elements either at the ordinary or higher temperatures: *chlorine, bromine, iodine, oxygen, sulphur, selenium, phosphorus, silicon, arsenic, antimony* (for details *v.* Copper, chloride of; bromide of, &c.). It is not quite certain whether Cu combines directly with *nitrogen* or not; Blondlot (*C. R.* 102, 210) got indications of combination when discs of Cu and Pt were strongly heated in an atmosphere of N (*cf.* Copper, nitride of).

Detection and Estimation. Cu salts in solution give a deep-blue colour with excess of NH_3Aq; a mahogany-coloured pp. of ferrocyanide of Cu in very dilute liquids. Minute traces of Cu may be detected by immersing a small couple of Zn and Pt wires in the liquid, and then exposing the Pt wire to the vapour given off by adding conc. H_2SO_4 to KBr; if a trace of Cu has been deposited on the Pt a deep-violet colour is produced, due to formation of a compound of $CuBr_2.xH_2O$ with HBr (Cresti, *G.* 7, 220). Copper is often estimated by ppn. with KOHAq, heating, and weighing as CuO; also by ppn. as metal by means of Zn and Pt. Volumetric methods of estimation are based on the reaction of ammoniacal Cu solutions with KCNAq to form colourless $Cu(CN)_2.2NH_4CN$; on the reaction of Cu solutions with KIAq to form Cu_2I_2, and I; on the reaction of Cu_2O with Fe_2Cl_6Aq to form $CuCl_2Aq$ and $FeCl_2Aq$; and on other reactions. Cu may also be estimated by electrolysis (*v.* Classen, *Quantitative Analyse durch Electrolyse* [Berlin, 1886]). For details of methods a *Manual of Analysis* must be consulted.

Copper, Alloys of.—Many alloys of Cu are much used in manufactures because of their malleability, hardness, and durability, and in some cases sonorousness. Only a brief account of the chief classes of these alloys is given here; for details of those alloys which are of especial technical importance reference must be made to the *Dictionary of Technical Chemistry.*

1. With *aluminium.* Alumina and CuO are strongly heated with carbon in about the ratio Al:9CuO:9C. The alloy which results has the composition Cu_9Al; it has the colour of gold, is very tenacious and malleable, very hard, and takes a high polish. This alloy, or an alloy containing from 5 to 10 p.c. Al, is generally known as *aluminium-bronze* (*v.* Debray, *C. R.* 43, 925).

2. With *antimony.* Cu and Sb alloy in almost all proportions. Compounds $SbCu_2$ and $SbCu_4$ probably exist (*v.* Ball, *C. J.* 53, 167). These alloys are brittle. Sb is present in many varieties of bronzes and in alloys for making parts of locomotives. For action of acids on alloys of Sb and Cu *v.* Calvert a. Johnson, *T.* 1858. 319.

3. With *arsenic*; *v.* Copper, arsenides of.

4. With *bismuth*; various alloys are formed by heating the metals together; an alloy of 2 parts Bi with 1 part Cu expands after solidification (Marx, *S.* 58, 470).

5. With *gold v.* Roberts, *A. Ch.* [5] 13, 133.

6. With *iron.* Cu is alloyed with iron by fusion. (For description of alloys *v.* Mushet, *P. M.* (3) 6, 81.)

7. With *lead.* Cu and Pb melted together at a red heat form alloys; but the fused mass tends to separate into two layers; the upper containing much Cu and little Pb, and the lower much Pb and little Cu; separation is partly prevented by rapid cooling. Pb is found in many clock-metals and bronzes.

8. With *nickel.* Alloys of Cu and Ni, with about 10Cu and 4Ni, are nearly white; alloys containing Cu, Ni, and Zn are largely used under the names of *German silver, Packfong,* &c.

9. With *silver*; Cu and Ag alloy in very varied proportions (for details *v.* Roberts, *A. Ch.* (5) 13, 111).

10. With *tin.* The various bronzes, gun-metals, and bell-metals, are alloys of Cu and Sn; these alloys are formed by fusing the two metals together. Many bronzes contain Pb, and some contain small quantities of Fe and Sb. For details of the manufacture and properties of the copper-tin alloys *v. Dictionary of Technical Chemistry.* Two compounds of Cu and Sn appear to exist, Cu_4Sn and Cu_3Sn; the evidence is based on the variations in the specific gravities, electrical conductivities, and other physical properties, of the alloys of Cu and Sn (*v.* Matthiessen, *T.* 1860. 161; Riche, *C. R.* 55, 1862; Lodge, *P. M.* (5) 8, 554; Calvert a. Johnson, *T.* 1858. 319; Roberts, *P. M.* (5) 8, 58, 551; Laurie, *C. J.* 53, 104; Ball, *C. J.* 53, 167).

11. With *zinc* Ordinary brass is an alloy of about 2 parts Cu to 1 part Zn; many alloys of the two metals in various proportions are used in manufactures under the names of *Pinchbeck, Mosaic gold,* &c. Modern bronze is generally an alloy of Cu with *zinc* and *tin.* These alloys are formed either by fusing the metals together, or by heating Cu with ZnO and charcoal. In some cases one metal is ppd. on the other from solution. For details regarding the manufacture, properties, and uses of the various brasses, &c., *v. Dictionary of Technical Chemistry.* There are indications of the formation of a compound of Cu and Zn, *viz.* $CuZn_2$ (*v.* Laurie, *C. J.* 53, 104). For action of acids on Cu-Zn alloys *v.* Calvert a. Johnson, *C. J.* [2] 4, 435; also Matthiessen, *C. J.* [2] 4, 502.

Copper, Antimonate of. $Cu(SbO_3)_2.5H_2O$ (Fremy, *A. Ch.* [3] 12, 499; Heffter, *P.* 86, 418).

Copper, Antimonides of (*v.* Copper, alloys of).

Copper, Arsenates of. $Cu_5H_2(AsO_4)_4.2H_2O$, and $Cu_3(AsO_4)_2$ (*v.* Arsenic, acids of, vol. i. 308).

Copper, Arsenides of. The compounds Cu_3As, Cu_6As, and Cu_9As, occur native as *Domeykite, Algodonite,* and *Darwinite,* respectively. According to Lippert (*J. pr.* 81, 168) the grey deposit obtained by heating Cu in an HCl solution of As_2O_3 in Cu_5As_2; when this is heated in H, Cu_6As remains.

Copper, Arsenites of. $CuHAsO_3$, and $Cu(AsO_2)_2$; *v.* Arsenic, acids of, vol. i. 306.

Copper, Boride of. When amorphous B is heated with Cu in a crucible for some hours, above the M.P. of Cu, a yellow, very hard, brittle, mass is obtained, S.G. 8·116; this is Cu_3B_2 according to Marsden (*C. J.* 37, 672).

Copper, Borofluoride of. $Cu(BF_4)_2$, *v.* under Copper, fluorides of.

Copper, Bromides of. Two bromides are known, $CuBr_2$, and Cu_2Br_2 (or CuBr). The molecular weight of neither in the gaseous state has been determined; but judging from the chlorides the formulæ given are probably molecular. Thomsen gives the thermal values $[Cu^2,Br^2] = 49,970$; $[Cu,Br^2] = 32,580$; $[Cu^2Br^2,Br^2] = 15,190$; $[Cu,Br^2,Aq] = 40,830$ (*Th.* 3, 319).

I. Cupric bromide, $CuBr_2$. (*Copper dibromide.*) Prepared by dissolving $Cu(OH)_2$ in HBrAq, or digesting Cu turnings with excess of BrAq, or adding KBrAq to $CuSiF_6Aq$; the green solution turns brown on evaporation; when the residue is gently heated, $CuBr_2$ remains as a graphite-coloured fusible mass. If the green solution is evaporated *in vacuo* over H_2SO_4, $CuBr_2$ is obtained in lustrous iodine-coloured crystals (Rammelsberg, *P.* 55, 246). By evaporating in air, Berthemot (*A. Ch.* 44, 385; *v.* also Lowig, *P.* 14, 485) obtained greenish-brown crystals of $CuBr_2.5H_2O$. $CuBr_2$ is deliquescent and very soluble in water; when heated it gives CuBr and Br. This bromide combines with ammonia to form $CuBr_2.5NH_3$ and $CuBr_2.3NH_3$; the former is a blue powder obtained by passing NH_3 over $CuBr_2$; the latter forms dark-green crystals, obtained by adding alcohol to $CuBr_2Aq$ saturated with NH_3 (Rammelsberg, *P.* 55, 246). These double compounds dissolve in water; on dilution $Cu(OH)_2$ is ppd.; when heated they give off NH_3 and NH_4Br and leave a mixture of $CuBr_2$ and CuO.

II. Cuprous bromide. Cu_2Br_2. (*Copper monobromide.*) Prepared by heating $CuBr_2$, by passing Br over heated Cu, or by reaction between Cu and $CuBr_2Aq$ mixed with $FeBr_2Aq$ (Renault, *C. R.* 59, 319). A white powder, insoluble in water. S.G. 4·72; M.P. = 504°; B.P. between 861° and 954° (Carnelley a. Williams, *C. J.* 37, 125). Not decomposed by conc. H_2SO_4, but by HNO_3Aq (Berthemot, *A. Ch.* [2] 44, 385; Löwig, *P.* 14, 485). Turns bluish in sunlight and is then less soluble than before in NaClAq or $Na_2S_2O_3Aq$ (Renault, *C. R.*, 59, 319).

Copper, Chlorides of. Two chlorides of copper are known, $CuCl_2$ and CuCl or Cu_2Cl_2. Many experiments have been made on the V.D. of cuprous chloride; it is very probable that the molecular formula of this salt is Cu_2Cl_2. Thomsen gives the thermal data $[Cu^2,Cl^2] = 65,750$; $[Cu,Cl^2] = 51,630$; $[Cu, Cl^2,2H^2O] = 58,500$; $[CuCl^2,2H^2O] = 6,870$; $[Cu,Cl^2,Aq] = 62,710$ (*Th.* 3, 319).

I. Cupric chloride. $CuCl_2$. (*Copper dichloride.*)

Preparation.—1. By burning Cu in Cl gas, or by passing Cl over heated CuCl.—2. By dissolving Cu in *aqua regia*, or in boiling conc. HClAq in presence of air, or by dissolving CuO or $CuCO_3$ in hot HClAq; the green solutions thus obtained are evaporated and the crystals of $CuCl_2.2H_2O$ which form are heated to 100°.—3. By mixing NaClAq with $CuSO_4Aq$, evaporating, filtering from Na_2SO_4, evaporating, and heating the $CuCl_2.2H_2O$ obtained.

Properties and Reactions.—A brownish-yellow, deliquescent, solid; melts at red heat and gives CuCl and Cl. Easily soluble in water, solution in a very little water is dark-green (Solly, *P. M.*, 1843. 367); on addition of more water it becomes green, colour of very dilute solutions is greyish-blue (Gladstone, *C. J.* 8, 211, says that $CuCl_2.2CuO.4H_2O$ is formed); addition of conc. HClAq or better H_2SO_4 produces a yellow colour in a green solution of $CuCl_2$. Franz (*J. pr.* [2] 5, 274) gives the following data showing the composition and S.G. of $CuCl_2Aq$: —

P.c. $CuCl_2$	S.G.	P.c. $CuCl_2$	S.G.
5	1·0155	25	1·2918
10	1·092	30	1·3618
15	1·1565	35	1·1147
20	1·2223	40	1·5284

$CuCl_2$ is soluble in alcohol and in ether; alcoholic solutions burn with green flame. $CuCl_2Aq$ ppd. by KOHAq yields various oxychlorides (*v.* Copper, oxyhaloid compounds of). For reactions of $CuCl_2$ with *metallic sulphides*, *v.* Rammelsberg (*C. J.* 39, 374), and Raschig (*A.* 228, 1).

Combinations.—1. With *water* to form $CuCl_2.2H_2O$; obtained by evaporating solutions of $CuCl_2$ and crystallising (*v. supra*); rhombic prisms $a:b:c = \cdot9179:1:\cdot4627$ (*Gm.-K.* [6th ed.] 3, 642); lose $2H_2O$ at 100°, or over H_2SO_4 (*cf.* Vogel, *D. P. J.* 136, 239, with Graham, *A.* 29, 31).—2. With *ammonia* to form $M.2NH_3$, $M.4NH_3.H_2O$, and $M.6NH_3$ $[M = CuCl_2]$ (Kane, *A. Ch.* 72, 273; Rose, *P.* 20, 155). $CuCl_2.6NH_3$ is formed by passing NH_3 over $CuCl_2$ as long as absorption continues; when heated to 149°, NH_3 is evolved and $CuCl_2.2NH_3$ remains. When NH_3 is passed into hot conc. $CuCl_2Aq$ until the pp. which forms has re-dissolved, and the liquid is allowed to cool, $CuCl_2.4NH_3.H_2O$ separates in dark-green octahedra which lose NH_3 on drying.—3. With *ammonia and salammoniac* to form $CuCl_2.2NH_3.2NH_4Cl$; obtained by boiling Cu turnings with conc. NH_4ClAq till a deep-blue liquid is obtained, filtering from $Cu_2Cl_2.2NH_3$ which separates, allowing the filtrate to oxidise in the air until it becomes greenish, and cooling (Ritthausen, *J. pr.* 60, 376). Dark-green tablets, decomposed by water.—4. With *cuprous chloride and ammonia* to form $CuCl_2.Cu_2Cl_2.4NH_3.H_2O$ (Ritthausen, *J. pr.* 60, 374); obtained by dissolving Cu_2Cl_2 in NH_3Aq, allowing the solution to become deep blue by exposure to air, and crystallising; or by the prolonged action of NH_4ClAq on Cu turnings at the ordinary temperature. Blue prisms; decomposed by water and alcohol; absorb O from air and lose NH_3; when heated leave Cu_2Cl_2; soluble in hot HClAq from which solution $CuCl_2.2NH_4Cl.2H_2O$ crystallises out.—5. With *ammonium chloride*, to form (a) $CuCl_2.2NH_4Cl.2H_2O$, and (b) $CuCl_2.NH_4Cl.2H_2O$. The former is obtained by crystallising a mixed solution of the two salts (Mitscherlich, *J. pr.* 19, 419; Graham, *A.* 29, 132); or by concentrating a mixed solution of $CuSO_4$ and NH_4Cl (Vogel, *J. pr.* 2, 194); or saturating $CuCl_2Aq$ with NH_3 (Cap a. Henry, *J. pr.* 13, 184). Light-blue rhombic tables, or octahedra; loses all H_2O at 110°–120°; S.G. 1·96 to 1·97. The salt $CuCl_2.NH_4Cl.2H_2O$ was obtained by Hantz (*A.* 66, 280), as blue-green crystals, by neutralising 1 part HClAq by NH_3 and 2 parts of the same HClAq by $CuCO_3$, mixing the solutions, and crystallising.—6. With *potassium chloride* to form $CuCl_2.2KCl.2H_2O$; obtained by evaporating a mixed solution of the two salts. S.G. 2·4.

II. Cuprous Chloride. Cu_2Cl_2. (*Protochloride of copper.*) Mol. w. 197·14. V.D. (c. 1560°) 6·8. Formula found to be Cu_2Cl_2 and not CuCl from results of V.D. determinations by V. and C. Meyer, at c. 1560° (*B.* 12, 1112, 1283). $[Cu^2, Cl^2] = 65,750$; $[Cu^2Cl^2, Cl^2] = 37,510$ (*Th.* 3, 319).

Formation.—1. Cu is heated in Cl, keeping the Cu in excess.—2. Cu is heated to dull redness in a stream of HCl (Wohler, *A.* 105, 360).—3. By heating together $CuCl_2$ and Cu in HClAq.—4. By heating together Cu and Fe_2Cl_6Aq. 5. By heating $CuCl_2$. 6. By reducing $CuCl_2Aq$ or $CuSO_4Aq$ by $SnCl_2$, or SO_2.—7. By heating 2 parts $HgCl_2$ with 1 part Cu turnings.—8. By heating $CuSO_4$ with NaH_2PO_2 in a little water (Cavazzi, *G.* 16, 167).

Preparation.—1. Sulphur dioxide is passed into a mixture of 1 part NaCl and $2\frac{1}{2}$ parts $CuSO_4.5H_2O$ dissolved in water; the white pp. is washed with SO_2Aq, then with glacial acetic acid, pressed between paper, and dried at 100° (Wohler, *A.* 130, 373; Rosenfeld, *B.* 12, 951). $[2CuCl_2Aq + H_2SO_3 + H_2O = Cu_2Cl_2 + H_2SO_4Aq + 2HClAq]$.—2. An intimate mixture of 14·2 parts powdered CuO with 7 parts zinc powder is thrown, little by little with constant shaking, into conc. HClAq, until a white pp. of Cu_2Cl_2 begins to form; more acid is added, and then a little more of the mixture, and so on until the whole of the mixture has been used. The liquid is then poured into boiled water in a flask so that the flask is filled; the flask is closed; the Cu_2Cl_2, which separates as a shining white solid, is washed with distilled water, and dried in the dark (Heumann, *B.* 7, 720). $[2CuO + Zn + 4HClAq = Cu_2Cl_2 + ZnCl_2Aq + 2H_2O]$.

Properties.—Snow-white crystalline powder; insoluble in water, alcohol, dilute HNO_3 or H_2SO_4Aq; soluble in hot HClAq, separating on cooling in tetrahedra; soluble in NH_3Aq; soluble, on heating, in KClAq, NaClAq, Fe_2Cl_6Aq, $ZnCl_2Aq$, and many other metallic chlorides; soluble in $Na_2S_2O_3Aq$ when the two salts are in the ratio $Cu_2Cl_2:Na_2S_2O_3$ (Winkler, *J. pr.* 88, 128). S.G. 3·7. Melts below red heat, and boils between 954° and 1032° (Carnelley a. Williams, *C. J.* 37, 126). Solution in HClAq acts as an energetic reducer, converting $HgCl_2$ to HgCl, $AuCl_3$ to Au, decolourising Prussian blue, &c.; this solution rapidly absorbs CO (*v.* Hempel, *B.* 21, 898; *cf.* Drehschmidt, *B.* 21, 2158), colourless crystals of $Cu_2Cl_2.CO.2H_2O$ separate from a saturated solution of CO in Cu_2Cl_2 (Berthelot, *A. Ch.* [3] 46, 488), on warming the solution CO escapes. This solution also absorbs various gases, *e.g.* C_2H_2 and PH_3 (Riban, *B.* 12, 1208; Rose, *P.* 4, 110; 6, 205).

Reactions.—1. Moist Cu_2Cl_2 changes in *sunlight* and *air* to yellow, violet, and then blue-black; an oxychloride is formed ($CuCl_2.3CuO$, according to Vogel, *D. P. J.* 136, 238) [concerning the action of sunlight on Cu_2Cl_2 *v.* Carlemann, *J. pr.* 63, 475].—2. Heated in *oxygen* or in *water-vapour*, CuO is formed.—3. By repeated washing with *water* $CuCl_2$ and Cu_2O are produced.—4. Reduced to Cu by *hydrogen*, or by digestion under water with *iron filings*. —5. Scarcely acted on by *sulphuric acid*, even when conc. and hot (Rosenfeld, *B.* 12, 954).—6. Reacts with many *metallic sulphides* to produce Cu_2S (*v.* Raschig, *A.* 228, 1).

Combinations.—1. With *ammonia* to form $Cu_2Cl_2.2NH_3$. By dissolving Cu_2Cl_2 in NH_3Aq; or better by boiling Cu turnings with conc. NH_4ClAq until rapid evolution of NH_3 begins, filtering the boiling liquid into ½ its volume of water, and repeatedly filtering from $Cu_2O.xH_2O$, allowing to cool, repeatedly washing the solid which separates with alcohol and quickly pressing between paper (Ritthausen, *J. pr.* 59, 369, Millon a. Commaille, *C. R.* 56, 309). Colourless rhombic dodecahedra, becoming violet in air; decomposed by water into its constituents on heating; solution in water reduces ammoniacal silver solutions (M. a. C.), it absorbs O from the air forming $Cu_2Cl_2.CuCl_2.4NH_3.H_2O$ (*q.v.* under CUPRIC CHLORIDE, *Combinations*, No. 4).—2. With *salammoniac* to form $Cu_2Cl_2.4NH_4Cl$. Obtained by dissolving $Cu_2Cl_2.2NH_3$ in HClAq, or by adding a little NH_3Aq to Cu_2Cl_2 in HClAq; white crystals, becoming brown in air, and giving Cu_2Cl_2 and NH_4Cl when heated (Ritthausen, *J. pr.* 59, 369). —3. With *potassium chloride* to form $Cu_2Cl_2.4KCl$; large octahedra; prepared by dissolving Cu_2Cl_2 in boiling KClAq, and allowing to cool in a closed vessel (Mitscherlich, *A. Ch.* 73, 384). A compound with NaCl is also known; it is very soluble and difficult to crystallise.—4. With *phosphorus hydride*, to form $Cu_2Cl_2.2PH_3$. Obtained, as long colourless needles, by passing PH_3 into Cu_2Cl_2 in HClAq until crystals form; when heated gives Cu phosphide, PH_3, and HCl; water forms PH_3 and Cu_6P_2 (Riban, *Bl.* [2] 31, 385).

Copper, Fluorides of. Two fluorides have been isolated, CuF_2 and Cu_2F_2 (Berzelius, *P.* 1, 28).

I. CUPRIC FLUORIDE, $CuF_2.2H_2O$. Best obtained by dissolving $CuCO_3$ in HFAq, and adding alcohol of 95 p.c. (Balbiano, *G.* 14, 74). Pale-blue crystalline powder; sparingly soluble in water, very easily decomposed to oxyfluoride $CuF_2.Cu(OH)_2$[$=CuF.OH$] (*v. Oxyfluoride* under COPPER, OXYHALOID COMPOUNDS OF). Decomposes on keeping for four or five days with evolution of HF. Combines with KF to form very soluble $CuF_2.2KF$. Absorbs NH_3 with formation of $CuF_2.Cu(OH)_2.4NH_3.2NH_4F.2H_2O$ (Balbiano, *l.c.*).

Cupric borofluoride $Cu(BF_4)_2$[$=CuF_2.2BF_3$] is obtained by mixing $Ba(BF_4)_2$ and $CuSO_4Aq$.

Cupric silicofluoride $CuSiF_6.6H_2O$ is produced by dissolving CuO in H_2SiF_6Aq and evaporating.

II. CUPROUS FLUORIDE, Cu_2F_2. A red powder obtained by treating $Cu_2O.xH_2O$ with HFAq; washing with water, pressing, and drying *in vacuo*; decomposed by moist air to $Cu(OH)_2.CuF_2$ (Berzelius, *l.c.*).

Copper, Hydride of. A compound of Cu and H is said to be produced by the following reactions:—1. 1 pt. $Ba(H_2PO_2)_2$ is dissolved in water, the Ba is exactly ppd. by H_2SO_4Aq, the filtrate is added to ·8 parts $CuSO_4.5H_2O$ in rather dilute solution, at the ordinary temperature, ppn. is allowed to proceed slowly; the pp. is washed with air-free water in an atmosphere of CO_2, and dried by pressure between paper (Wurtz, *A. Ch.* [3] 11, 250; *C. R.* 89, 1066; 90, 22).—2. $NaHSO_2Aq$ is added in excess to $CuSO_4Aq$; if the $CuSO_4$ is in excess the pp. contains some Cu (Schutzenberger, *C. R.* 69, 196).—3. Zinc is placed in $CuSO_4Aq$ acidulated with H_2SO_4 (Schoor, *Ar. N.* 12, 96; [*J.* 1877. 273]).—4. A moderately strong current is passed through very dilute slightly acidulated $CuSO_4Aq$; the compound forms at the negative pole but begins to decompose, with evolution of H, as soon as the current is stopped (Poggendorff, *P.* 75, 337). Copper hydride is described as a reddish-brown powder, having the composition Cu_2H_2; it decomposes at 60° into Cu and H; in HClAq it gives Cu_2Cl_2 and H; it takes fire in Cl. (*Cf.* Berthelot [*C. R.* 89, 1005, 1097], who says that the so-called copper hydride always contains O, H_2O, and P; but Wurtz [*C. R.* 90, 22] gives further details and analyses, showing that the preparation is apt to contain Cu phosphate, but the presence of more than a mere trace of this may be avoided by ppg. the Cu_2H_2 very slowly in cold solutions.)

Copper, Hydroxides of, *v.* HYDRATED OXIDES OF COPPER, under COPPER, OXIDES OF.

Copper, Iodides of. Only one iodide of copper has been isolated; this is the cuprous compound, Cu_2I_2. When KIAq is added to the solution of a cupric salt, a pp. of Cu_2I_2 mixed with free I is obtained; *e.g.* $2CuSO_4Aq + 4KIAq = Cu_2I_2 + I_2 + 2K_2SO_4Aq$. Cu_2I_2 dissolves in alcoholic solution of I; the liquid is not ppd. by water, but on heating and adding alcoholic solution of KI, Cu_2I_2 is ppd. along with KI_3. Solutions containing about 3 gram CuI_2 per 100 c.c. have been obtained; compounds are known which probably contain CuI_2 (*v. infra*).

CUPROUS IODIDE, Cu_2I_2. S.G. 4·41 (Schiff). B.P. between 759° and 772° (Carnelley a. Williams, *C. J.* 37, 126). Mol. w. not determined, but from analogy of Cu_2Cl_2 it is probably Cu_2I_2 $=379·46$. $[Cu^2,I^2]=35,200$ (*Th.* 3, 319).

Formation.—1. Finely divided Cu heated with I forms Cu_2I_2; a plate of Cu exposed to the vapour of I becomes covered with crystals of Cu_2I_2 (Renault, *C. R.* 59, 319).—2. Cu is dissolved in conc. HIAq, on standing in air (or better on adding a trace of H_2S) Cu_2I_2 ppts. in crystals (Rose, *P.* 4, 110).—3. Cu_2S is dissolved in conc. HIAq (Mensel, *B.* 3, 123).—4. KIAq is added to $CuSO_4Aq$; Cu_2I_2 is ppd. along with I.

Preparation.—$CuSO_4Aq$ is saturated with SO_2, or a mixture of 1 pt. $CuSO_4.5H_2O$ and $2\frac{1}{4}$ pts. $FeSO_4.7H_2O$ is dissolved in water, KIAq is added, the pp. is washed and dried (Duflos, *A.* 39, 253; Soubeiran, *J. Ph.* 13, 427).

Properties and Reactions.—A white, or brownish-white, crystalline powder; insoluble in water, alcohol, and dilute acids; soluble in KIAq, and in NH_3Aq in presence of air. Soluble in hot conc. HClAq and reppd. on addition of water. Decomposed by conc. HNO_3 or H_2SO_4. Heated with MnO_2 or $KClO_3$, CuO is formed; reduced to Cu by boiling with water and Zn, Sn, or Fe (Berthemot, *J. Ph.* 15, 445). When Cu_2I_2 is dissolved in NH_3Aq by heating in an open vessel, colourless crystals of $Cu_2I_2.4NH_3$ separate on cooling, and the mother liquor on addition of alcohol deposits a dark-blue compound $CuI_2.4NH_3.H_2O$ (Rammelsberg, *P.* 48, 162; *v.* also Berthemot, *J. Ph.* 15, 415; and Saglier, *C. R.* 102, 1552). Cu_2I_2 dissolves in alcoholic I; when this liquid is heated to 30°, and mixed with alcoholic NH_3 at 30°, crystals separate in a few hours having the composition $CuI_2.4NH_3.I_2$ (Jörgensen, *J. pr.* [2] 2, 353).

Combinations.—1. With *ammonia* to form $Cu_2I_2.4NH_3$ (Rammelsberg, *P.* 48, 162). Obtained by passing NH_3 over Cu_2I_2; white, lustrous crystals; decomposed by heat to Cu_2I_2 and NH_3. The same compound is formed by mixing KIAq with an ammoniacal solution of a cuprous salt in absence of air; as thus obtained the compound cannot be dried without losing NH_3 (Levol, *N. J. P.* 4, 328).—2. With *ammonium iodide*; the compound $Cu_2I_2.2NH_4I.H_2O$ is obtained, as white needles, by dissolving 100 gs. NH_4I in 1,000 gs. water, adding 10-15 gs. $Cu(OH)_2$, heating until all is dissolved, boiling with a large excess of Cu until the liquid is colourless, and allowing to cool. The mother liquor in air deposits black crystals of $Cu_2I_2.2NH_4I.2NH_3.4H_2O$. These crystals are very unstable (Saglier, *C. R.* 104, 1440).—3. With *ammonia and cupric iodide*; when 100 gs. of an ammoniacal solution of CuO, containing 7-8 p.c. CuO, is mixed with an equal mass of 10 p.c. alcoholic I solution, warmed until the pp. of NI_3 dissolves, heated in the water bath for an hour, and allowed to cool, brilliant green crystals are deposited of the composition $Cu_3I_4.4NH_3$, probably $= Cu_2I_2.CuI_2.4NH_3$ (Saglier, *C. R.* 102, 1552).—4. With *silver iodide* to form a series of bodies resembling alloys; $Cu_2I_2.xAgI$, x varying from 1 to 12; for physical constants of these bodies *v.* Rodwell, *Pr.* 33, 143; Bellati a. Romanese, *Pr.* 34, 104. According to Guyard (*Bl.* [2] 41, 12) a double iodide of Cu and N is produced when an alkaline di-iodide is added to an ammoniacal Cu solution.

II. CUPRIC IODIDE. Cupric iodide, CuI_2, has not been isolated. A solution of Cu_2I_2 in alcoholic I is not ppd. by water, but on heating and adding alcoholic KI, Cu_2I_2 is reppd. along with KI_3, the solution may perhaps contain a periodide of Cu (Jörgensen, *J. pr.* [2] 2, 347). Cu_2I_2 in presence of I dissolves in much water; this solution probably contains CuI_2 (Traube, *B.* 17, 1064). Carnegie (*priv. comm.*) has obtained aqueous solutions of cupric iodide containing c. ·3 g. CuI_2 in 100 c.c., by digesting Cu_2I_2 with I in water at 80° for a few minutes, cooling, shaking *for a short time* with Cu foil or CS_2 to remove excess of I. Solution of CuI_2 containing c. ·9 g. CuI_2 with excess of I is very easily decomposed, almost anything that removes the I at the same time decomposes the CuI_2 to CuI and I, *e.g.* starch or Ag leaf; the solution partially decomposes when boiled out of contact with air, also when a current of air, N, or other indifferent gas, is passed through it, and even when kept *in vacuo* at the ordinary temperature. Solutions of CuI_2 are also obtained by digesting CuO_2H_2, or $CuCO_3$, with fairly conc. HIAq saturated with I, and filtering from excess of CuO_2H_2, or $CuCO_3$. Potassium iodide withdraws I from solutions of CuI_2, ppg. CuI; when KI interacts with a cupric salt in molecular proportions, CuI_2 is almost certainly produced, but as the change is not complete the residual KI interacts with the CuI_2 in solution to produce CuI and $KI.xI$. Thomsen gives $[Cu,I^2,Aq] = 10,410$ (*Th.* 3, 320).

Various compounds are known, one constituent of each of which is probably CuI_2. The formation of the compounds $CuI_2.4NH_3.H_2O$, and $CuI_2.Cu_2I_2.4NH_3$ has been described (*v.* CUPROUS IODIDE, *Reactions*, also *Combinations*, No. 3). The compound $CuI_2.4NH_3.I_4$ was obtained by Jorgensen (*J. pr.* [2] 2, 353) as blue crystals, by mixing solutions of I in KI and Cu NH_4 nitrate, at 50°, and filtering hot into water at 50° (*v.* also Saglier, *C. R.* 102, 1552). Saglier (*C. R.* 104, 1410) describes the compounds $CuI_2.2NH_4I.2NH_3.2H_2O$, and $CuI_2.4NH_3.H_2O$, produced by boiling NH_4IAq with $Cu(OH)_2$; he also describes a compound with $(NH_4)I_2$, viz. $CuI_2.2NH_4I_2.2NH_3.6H_2O$, obtained by dissolving $Cu(OH)_2$ in hot NH_4I_2Aq.

Carnegie (*priv. comm.*) has obtained the compound $CuO.2CuI_2.4H_2O$ by partially immersing slips of Cu in BaI_2Aq; black crystals slowly form on the sides of the vessel; they are easily decomposed by washing with water; they may be washed with alcohol and dried over $CaCl_2$.

Copper, Nitride of. Cu_3N. When finely divided CuO, ppd. from hot $CuSO_4Aq$ by KOH, is heated in a tube to 250° and dry NH_3 is passed over it, greenish-black copper nitride is formed; if the solid is powdered from time to time and the passage of NH_3 is continued, the whole of the CuO may be changed to nitride. Copper nitride decomposes by heating to about 300°, giving Cu and N; in Cl it gives $CuCl_2$ and N; in HClAq, $CuCl_2$, and NH_4Cl are formed; it is oxidised rapidly by HNO_3Aq, and decomposed to Cu and N by H_2SO_4Aq (Schrötter, *A.* 37, 136; *v.* also Warren, *C. N.* 55, 155). By heating to bright redness discs of Cu and Pt placed 3-4 mm. apart in an atmosphere of N, Blondlot got indications of the formation of a compound of Cu and N; but he did not isolate the compound (*C. R.* 102, 210). According to Schrotter (*l.c.*) Cu and N do not directly combine.

Copper, Oxides of. Copper forms four oxides; Cu_4O, Cu_2O, CuO, and CuO_2. There are indications of the existence of other oxides, but none has been certainly isolated. The best-studied are Cu_2O and CuO; both are basic, and each forms a series of corresponding salts, those corresponding to CuO being the more stable. The oxide Cu_4O reacts with acids to form Cu and a salt, in some cases a cuprous, and in other cases a cupric, salt. The oxide CuO_2 reacts with acids as a basic peroxide, forming cupric salts and oxygen. Any oxide other than CuO is changed into CuO by heating in air or oxygen. By adding solution of bleaching powder to $Cu2NO_3Aq$, a pp. is obtained which soon decomposes with evolution of O; this pp. is possibly a salt the acidic radicle of which is composed of Cu and O (*v.* p. 260). No oxide of Cu has been gasified, hence the formulæ given are not necessarily molecular.

I. Copper suboxide Cu_4O. (*Quadroxide of copper*) (Rose, *P.* 120, 1). An olive-green powder; stable under water in absence of O, but rapidly oxidised in air to Cu_2O and then to CuO; decomposed by dilute HClAq to Cu_2Cl_2 and Cu, and by dilute H_2SO_4Aq to $CuSO_4$ and Cu; insoluble in NH_3Aq, and in a mixture of NH_3Aq and $(NH_4)_2CO_3Aq$. Prepared by reaction between $CuSO_4Aq$ and $SnCl_2$ in presence of KOH; $Cu(OH)_2$ is first precipitated and then reduced with simultaneous formation of K stannate: $4Cu(OH)_2 + 12KOHAq + 3SnCl_2Aq$ $= Cu_4O + 6KClAq + 3K_2SnO_3Aq + 10H_2O$. To prepare this oxide, Rose directs to make 300 c.c. $CuSO_4Aq$ containing 10 g. Cu; to add this to 1,000 c.c. of a solution of 50 g. $SnCl_2$ in KOHAq, and to shake in a well-closed vessel which is completely filled with the liquid, keeping cool by water; to filter after twenty-four hours in an atmosphere of H, and wash the pp. with water containing KOH, then with water, then with very dilute NH_3Aq, and finally with water. It is difficult to obtain Cu_4O free from the other oxides. (For precautions *v.* Rose, *l.c.*)

II. Cuprous oxide Cu_2O. (*Hemi-oxide of copper. Protoxide of copper. Red oxide of copper.*) S.G. $_{4^\circ}$ 5·719 (native), 5·345-5·375 (artificial). H.F. $[Cu^2,O] = 40,810$ (*Th.* 3, 320). Occurs native as *Cuprite*, in lustrous, red, octahedra.

Formation.—1. By heating Cu in air; the outer film thus formed is CuO, beneath this is a film of Cu_2O. Finely divided Cu (obtained by reducing CuO in H at a moderate temperature) oxidises in air to Cu_2O (Berzelius, *A.* 61, 1; *v.* also Mitscherlich, *J. pr.* 19, 450; and Marchand, *J. pr.* 20, 505).—2. By heating Cu turnings with CuO (Berzelius), or with dehydrated $CuSO_4$ (Ullgren, *P.* 55, 527), or with $CuSO_4$ and Na_2CO_3 (Malaguti, *J. pr.* 2, 167).—3. By heating Cu_2Cl_2 with Na_2CO_3 (Wohler a. Liebig, *P.* 21, 581).—4. By the reaction of Cu with $Cu2NO_3$ and a little CuO, in absence of air (Becquerel, *A. Ch.* 41, 223).—5. By the prolonged action of NH_3Aq on a mixture of $CuSO_4Aq$ and $FeSO_4Aq$ in presence of $Fe_2(OH)_6$ (Wibel, *Reduction von Kupferoxydsalzen* [Hamburg, 1864], 2).

Preparation.—1. 5 pts. Cu_2Cl_2 are heated with 3 pts. dehydrated Na_2CO_3, the resultant mass is washed with water (W. a. L., *P.* 21, 581).—2. A mixture of 1 pt. $CuSO_45H_2O$, 1½ pts. cream of tartar, 2 pts. grape sugar, in 12 pts. water, is heated in a basin; 1½ pts. NaOH are added, and the whole is boiled until the supernatant liquid is colourless; the pp. is washed with water, then with alcohol, and dried (Böttger, *D. P. J.* 171, 77).—3. An intimate mixture of equal parts CuO and $(NH_4)_2CO_3$ is heated over a Bunsen-burner till the smell of NH_3 is no longer apparent (Schiff, *W. J.* 1864. 274).

Properties.—A carmine-red crystalline powder. Melts at full red heat and oxidises to CuO. Soluble in NH_3Aq, forming a colourless liquid which becomes blue in the air, and reacts as a strong reducing agent.

Reactions.—1. *Hydrochloric acid* forms Cu_2Cl_2, soluble in excess of the acid $[Cu^2O,2HClAq] = 14,660$ (*Th.* 3, 320).—2. *Dilute acids, e.g.* H_2SO_4Aq, HNO_3Aq, H_3PO_4Aq, $H.H_3C_2O_2Aq$, produce Cu and cupric salts.—3. *Conc. nitric acid* forms $Cu2NO_3$.—4. *Bromine water* forms $CuBr_2$ and CuO.—5. Reduced to Cu by *hydrogen, potassium,* or *carbon.*—6. *Sulphur* forms Cu_2S.—7. Many *metallic chlorides in solution, e.g.* $MgCl_2Aq$, $ZnCl_2Aq$, form soluble double salts and also ppt. hydrated oxides of the metals.—8. *Ferric chloride* solution produces Fe_2O_3, Cu, and Cu_2Cl_2.—9. From neutral *silver solution* Cu_2O ppts. a mixture of Ag and a basic cupric salt.

Hydrated cuprous oxide ?$4Cu_2O.H_2O$. Produced, as a yellowish powder, by adding an alkali or alkaline carbonate to the solution of a cuprous salt (Fremy, *A. Ch.* [3] 23, 391). Also formed by heating to boiling moist $Cu(OH)_2$ with milk sugar and some Na_2CO_3Aq. According to Mitscherlich (*J. pr.* 19, 450) the hydrate loses its water at 360°. Oxidises in air to $Cu(OH)_2$ (*v.* also *Gm.-K.* [6th ed.] 3, 595; Millon a. Commaille, *C. R.* 57, 145; Field, *C. J.* [2] 1, 28; P. de Saint-Gilles, *A. Ch.* [3] 42, 36). Dissolves in dilute acids to form cuprous salts, very few of which have been isolated.

III. Cupric oxide CuO. (*Black oxide of copper. Copper oxide.*) S.G. 6·1 to 6·4 (Boullay, *A. Ch.* [2] 43, 266; Playfair a. Joule, *C. S. Mem.* 3, 57). H.F. $[Cu,O] = 37,160$ (*Th.* 3, 320). Occurs native in North America as *Melakonite*. Crystallises in monoclinic forms; $a.b:c = 1·49:1:1·36$ (Maskelyne, *B. A.* 1865).

Formation.—1. By heating Cu in air or O, removing the scales which form, and strongly heating in air.—2. By heating $Cu2NO_3$, $Cu(OH)_2$, $CuCO_3$, or very strongly heating $CuSO_4$.

Preparation.—1. Pure Cu, prepared by electrolysis, is dissolved in HNO_3Aq, to one-half of the solution NH_3Aq is added until the pp. which forms has just dissolved, the other half of the liquid is then added, the whole is evaporated to dryness, and the Cu nitrate thus obtained is strongly heated; the oxide thus formed is well washed, and again heated in a Pt dish (Reischauer, *J.* 1863. 274; Erdmann a. Marchand, *J. pr.* 31, 389). The oxide must not be too strongly heated else it partially fuses and contains Cu_2O; according to Thudichum a. Kingzett (*C. J.* [2] 15, 363) the oxide should be heated *in vacuo* to remove traces of CO_2.—2. A solution of equivalent masses of $CuSO_4.5H_2O$ and Na_2CO_3 is evaporated to dryness and the residue is heated strongly in a crucible and then well washed; moist air is then passed over the heated oxide to remove traces of chlorides (Stanford, *C. N.* 7, 81; Erlenmeyer, *Z.* 1863. 157). The oxide as thus prepared is specially adapted for use in organic analysis.—3. The oxide is obtained in crystals by dropping Cu_2Cl_2 in small successive quantities into a red hot Pt crucible (Schulze, *J. pr.* [2] 21, 413); Becquerel (*A. Ch.* 51, 122) obtained crystals of CuO by heating to dull redness

5 grams amorphous CuO with 2-3 grams pure KOH, washing with water, and separating the crystals by shaking.

Properties.—Brown-black amorphous powder; or metal-like, lustrous, monoclinic crystals. Hygroscopic (*v.* Rentzsch, *J. pr.* [2] 21, 413). Slightly volatile in a porcelain-oven (Elsner, *J.* 1866. 35). Said to lose O when strongly heated giving $CuO.2Cu_2O$ (Favre a. Maumené, *C. R.* 18, 658). According to Reischauer (*J.* 1859. 216) Cu_2O is formed by very strongly heating CuO; this is confirmed by Debray and Joannis (*C. R.* 99, 583) provided the heating is conducted *in vacuo*. According to Joannis (*C. R.* 102, 1157) CuO prepared at a high temperature develops less heat when dissolved in HClAq than specimens prepared at a low temperature. CuO is a basic oxide reacting with acids to form cupric salts CuX_2 [$X = NO_3$, $\frac{SO_4}{2}$, &c.]; it dissolves in much KOHAq, and perhaps forms salts in which CuO acts as an acidic radicle.

Reactions.—1. Easily reduced to Cu by heating in *hydrogen* or *carbon monoxide*, or with *carbon* or *carbon compounds* [hence its use in organic analysis] (for temperatures at which reduction in H and CO begins *v.* Wright a. Luff, *C. J.* 33, 1).—2. Heated with *copper* forms Cu_2O.—3. Heated with *phosphorus*, phosphide and phosphate of Cu are formed.—4. Heated with *sulphuretted hydrogen*, or with *sulphur in a stream of hydrogen*, Cu_2S is formed (Rose, *P.* 110, 120).—5. Heated with *sulphur* alone gives Cu_2S and SO_2 if S is in excess, or Cu_2O and $CuSO_4$ if CuO is in excess (Jordan, *J. pr.* 28, 222).—6. Heated with *salammoniac* Cu_2Cl_2 and a little $CuCl_2$ are formed. 7. Heating with *ferric chloride* produces Fe_2O_3 with $CuCl_2$ and Cu_2Cl_2 (Hunt, *C. R.* 69, 1357).—8. Reacts with *zinc-chloride* solution to produce a green powder $Zn_4Cu_5Cl_4.6H_2O$ (André, *C. R.* 106, 854).—9. Soluble in *ammonia*, also in *molten potash*.—10. *Acids* dissolve CuO with formation of cupric salts: Thomsen gives the following thermal data (M = CuO); [M,2HClAq] = 15,270; [M,H^2SO^4Aq] = 18,800; [M,$2HNO^3$Aq] = 15,250; [M,$2HClO^4$Aq] = 15,910; [M,$2C^2H^4O^2$Aq] = 13,180; [M,SO^3] = 42,170; [Cu,O,H^2SO^4Aq] = 55,960; [Cu,O,$2HNO^3$Aq] = 52,410.

Combinations.—1. With *water* to form $CuO.H_2O$, produced indirectly, *v. infra.*—2. With *water and ammonia* to form $xCuO.yNH_3.zH_2O$. CuO dissolves in NH_3Aq in presence of air, especially if a small quantity of an NH_4 salt is present (Berzelius). Kane (*A. Ch.* [2] 72, 283) obtained the compound $3CuO.4NH_3.6H_2O$ by adding NH_3Aq to $CuCl_2Aq$. Malaguti a. Sargeau (*A. Ch.* [3] 9, 438) obtained $CuO.4NH_3.4H_2O$ by treating with NH_3 the mother-liquor from the preparation of Cu-NH_4 chromate. A solution of CuO in NH_3Aq dissolves cellulose; the solution is conveniently prepared either by digesting Cu spirals with NH_3Aq in air, or by ppg. $CuSO_4Aq$ by the calculated quantity of NaOHAq, washing the pp. of $Cu(OH)_2$ and dissolving it in NH_3Aq (Schweizer, *J. pr.* 72, 109). Ammoniacal solutions of CuO are reduced with ppn. of Cu, by P, Zn, Co, &c.—4. With a few *metallic oxides* to form compounds of the type $CuO.xM_2O_3$; *e.g.* $CuO.Fe_2O_3$, formed by heating together the two oxides (List, *B.* 11, 1515), or by the reaction of CuO with Fe_2Cl_6Aq, or by ppg. by KOHAq a solution of equivalent masses of a Cu and a ferric salt. The compound $3CuO.Mn_2O_3$ is obtained by adding NaOH to an ammoniacal solution of CuO, and then $MnCl_2Aq$ drop by drop with constant stirring (Schneider, *Am.* 9, 269). The compound $CuO.Cr_2O_3$ is described by Persoz (*A. Ch.* [3] 25, 283).

HYDRATED CUPRIC OXIDE OR COPPER HYDROXIDE $CuO.H_2O = Cu(OH)_2$.

Preparation.—Obtained by adding dilute NaOHAq or KOHAq in slight excess to $CuSO_4Aq$; or preferably by adding $CuSO_4Aq$ to NaOHAq, keeping the latter in excess (Oglialoro, *J.* 1876. 217); washing very many times, and drying at a low temperature. Bottger (*J. pr.* 73, 491) recommends to drop NH_3Aq into boiling $CuSO_4Aq$ until the pp., which at first is greenish, becomes blue, to wash this pp. thoroughly, and then to add fairly conc. NaOHAq, keeping the temperature about 20°-40° (*v.* also Lowe, *D. P. J.* 149, 270; Péligot, *C. R.* 53, 209).

Properties.—A blue solid, sometimes crystalline, very easily dehydrated. Heated in presence of water it turns black, the change occurring more readily if KOH or NaOH is present; the black compound is $3CuO.H_2O$ according to Harms (*J.* 1857. 246), $6CuO.H_2O$ according to Rose (*P.* 84, 480). When heated to 100° it loses water, but it is not fully dehydrated even at 200°-300° according to Rose (*l.c.*; *cf.* Schaffner, *A.* 51, 168). The hydrate is soluble in acids, also in NH_3Aq, and in solutions of NH_4 salts; also in $Na_2S_2O_3Aq$ (Field, *C. J.* [2] 1, 28).

Reactions.—1. With *ferrous hydroxide* produces $Fe_2O_6H_6$ and $Cu_2O.xH_2O$ (Levol, *A. Ch.* 65, 320).—2. With *ferrous sulphate* solution produces $Cu_2O.xH_2O$ and basic ferric sulphate (Braun, *J.* 1867. 301).—3. Dissolves in *acids* to form cupric salts.—4. Dissolves in 4 to 6 parts *molten potash*; on adding water CuO is formed, but some of the Cu remains in solution, and on adding a large excess of KOHAq all dissolves.—5. Dissolves in *large excess* of *potash solution* to a blue liquid; according to Chodnew (*J. pr.* 28, 217) this liquid remains blue on boiling or on adding much water, but on standing in air for a long time a part of the Cu in solution is ppd. as $CuO.H_2O$; addition of HClAq to the blue liquid until nearly neutral ppts. $Cu(OH)_2$, but a little Cu remains in solution. Chodnew (*l.c.*) also states that addition of a large excess of KOHAq to $CuSO_4Aq$ or $Cu(NO_3)_2Aq$ causes some of the $Cu(OH)_2$ to dissolve; the solutions must be cold and dilute; the whole of the Cu is not ppd. on boiling. The hydrate dissolves in NaOHAq (70 p.c.), and gives a blue pp. on long standing, containing CuO and Na_2O according to Löw (*Fr.* 9, 463).

IV. COPPER PEROXIDE.—The oxide CuO_2 has not been obtained, but a hydrate $CuO_2.H_2O$ is known. This hydrate is prepared (1) by digesting finely-divided CuO, or $Cu(OH)_2$, with H_2O_2Aq for several days at 0° (Thénard; Krüss, *B.* 17, 2593); (2) by shaking very dilute $CuSO_4Aq$ with excess of $MnO_2.xH_2O$ or PbO_2, keeping cold (Schmid, *J. pr.* 98, 136); (3) by adding H_2O_2Aq to a solution of Cu-NH_4 sulphate (Weltzien, *A.* 140, 207). $CuO_2.H_2O$ is very easily decomposed with evolution of O; decomposition of the moist hydrate in presence of water begins at 6° (Krüss, *l.c.*). When quickly washed with *cold* water, pressed between paper, and then dried *in vacuo*, it is obtained pure. This hydrate forms an olive-green powder; it reacts with acids to give cupric salts and H_2O_2; dilute HClAq is said to produce a little O.

Oxides of copper other than Cu_4O, Cu_2O, CuO, and CuO_2. Different chemists have asserted the existence of oxides of the form $xCuO.yCu_2O$ intermediate between CuO and CuO_2, obtained either by strongly heating CuO, or by the action of hypochlorites on cupric salts in solution (*v.* Krüger, *P.* 62, 445; Crum, *A.* 55, 218; Fremy, *A. Ch.* [3] 12, 457; Krüss, *B.* 17, 2593). But according to Osborne (*Am. S.* [3] 32, 333) these bodies are all mixtures of CuO and Cu_2O; this result is confirmed by the experiments of Debray and Joannis on the dissociation of these mixtures (*C. R.* 99, 583), and by the thermal measurements made by Joannis (*C. R.* 100, 999).

Copper, oxybromide of, *v.* COPPER, OXYHALOID COMPOUNDS OF.

Copper, oxychlorides of, *v.* COPPER, OXYHALOID COMPOUNDS OF.

Copper, oxyfluoride of, *v.* COPPER, OXYHALOID COMPOUNDS OF.

Copper, oxyhaloid compounds of.—Several oxychlorides of the form $Cu_xCl_yO_z$ are known; an oxyfluoride $CuF_2.Cu(OH)_2$, and an oxyiodide $2CuI_2.CuO.4H_2O$, are also known; an oxybromide probably exists, but it has not been isolated.

COPPER OXYBROMIDE.—When a little NH_3Aq is added to $CuBr_2Aq$, a pale-green pp. is obtained, which becomes grey on heating; both of these bodies are oxybromides according to Löwig (*P.* 14, 485).

COPPER OXYCHLORIDES.—Various compounds of CuO with $CuCl_2$ are obtained by digesting $CuCl_2$ with $Cu(OH)_2$, also by the incomplete ppn. of $CuCl_2$ by alkalis, and also by the action of O on moist $CuCl_2$. The following are the chief oxychlorides:—

I. $CuCl_2.2CuO.4H_2O$; blue-green pp. by adding to $CuCl_2$ enough KOH to decompose $\frac{3}{5}$ of the $CuCl_2$; or by diluting $CuCl_2Aq$ until the liquid is blue (Gladstone, *C. J.* 8, 211). This oxychloride loses $3H_2O$ at 140°, leaving a chocolate-coloured monohydrate (Kane, *A. Ch.* 72, 277).

II. $2(CuCl_2.3CuO).7H_2O$; green pp. by adding excess of $NaC_2H_3O_2Aq$ to boiling $CuCl_2Aq$, or by the action of NaClAq on $Cu(C_2H_3O_2)_2$ (Casselmann, *Fr.* 4, 24). Also obtained by adding NH_3Aq, insufficient for complete decomposition, to a mixture of $CuSO_4Aq$ with excess of NaCl (Reindel, *J. pr.* 106, 378).

III. $CuCl_2.3CuO.4H_2O$; occurs native as *Atacamite*; used in the arts as *Brunswick green.* Prepared by the action of air on copper plates covered with HClAq or NH_4ClAq; or by digesting in air a mixture of NaCl, Cu turnings, and $CuSO_45H_2O$ with enough water to form a thick magma, or by exposing moist Cu_2Cl_2 to the air (Vogel, *D. P. J.* 136, 238; *v.* also Field, *P. M.* [4] 24, 123; Debray, *Bl.* [2] 7, 104).

COPPER OXYFLUORIDE $CuF_2.Cu(OH)_2$ [= CuF.OH] (Balbiano, *G.* 14, 74). A greenish-white solid obtained by adding to HFAq, CuO or $CuCO_3$ in quantity not sufficient to saturate the acid; or by mixing $CuSO_4Aq$ and KFAq.

COPPER OXYIODIDE $2CuI_2.CuO.4H_2O$; prepared by the action of Cu on BaI_2Aq in presence of air (*v. supra*, CUPRIC IODIDE).

Copper, oxysulphides of, $xCuS.yCuO$. When Na_2SAq is dropped into an ammoniacal solution of $CuSO_4$ at 70°-80° till the blue colour disappears, a pp. of 5CuS.CuO is formed; at higher temperatures the pp. contains more CuO, and at ordinary temperatures CuS is the product (Pelouze, *A. Ch.* [3] 17, 393). According to Maumené (*A. Ch.* [3] 18, 311) various oxysulphides are formed during the action of conc. H_2SO_4 with Cu, but this is negatived by the experiments of Pickering (*C. J.* [2] 18, 112).

Copper, phosphides of.—Two phosphides of copper are known, Cu_3P_2 and Cu_6P_2; another, Cu_2P_2, probably exists. The molecular weight of none of these compounds is known with certainty. Cu and P may be melted together in all proportions.

I. TRI-COPPER PHOSPHIDE Cu_3P_2. Obtained by passing PH_3 over warm $CuCl_2$, or by passing PH_3 into $CuSO_4Aq$ (H. Rose, *P.* 14, 188; 24, 328). According to Bottger (*J.* 1857. 107) the pp. produced by boiling P with $CuSO_4Aq$, and washing with $K_2Cr_2O_7Aq$ acidulated with H_2SO_4 (to remove basic Cu phosphate), has the composition Cu_3P_2. Prepared by the reaction of PH_3 with $CuCl_2$, the phosphide is a black solid, insol. HClAq, and loses half its P when strongly heated in H. Prepared by passing PH_3 into $CuSO_4Aq$, the phosphide is sol. HClAq with evolution of inflammable PH_3. Prepared by Böttger's method the phosphide is an easily oxidised powder, slowly dissolved by HClAq with evolution of non-inflammable PH_3 (*v.* also Sidot, *C. R.* 84, 1454).

II. HEXACOPPER PHOSPHIDE Cu_6P_2. Obtained by leading PH_3 over heated Cu_2Cl_2 or Cu_2S (H. Rose, *P.* 6, 209; 24, 328); by strongly heating Cu_3P_2 in H (Rose, *l.c.*); by passing P vapour over Cu heated to dull redness (Abel, *C. J.* [2] 3, 249). Grey-black solid, e. sol. HNO_3Aq, insol. HClAq.

A DI-COPPER PHOSPHIDE, Cu_2P_2, is described as a grey powder obtained by heating $CuHPO_4$ in a stream of H (H. Rose, *P.* 14, 188; 24, 328). Also produced by heating P with Cu turnings, and then carefully heating the product with amorphous P (Berzelius; but *cf.* Abel, *C. J.* [2] 3, 249). A phosphide, having the composition Cu_2P_2, was obtained by Cross a. Higgins (*C. J.* 35, 424) by heating Cu_2Cl_2Aq with amorphous P to 160° for many hours.

Copper, salts of. Compounds obtained by replacing H of acids by Cu. Copper forms two classes of salts, the *cuprous* Cu_2X_2 [X = Cl, Br, I, SCN, $\frac{SO_3}{2}$, &c.], and the *cupric* CuX_2 [X = Cl, NO_3, $\frac{SO_4}{2}$, $\frac{CO_3}{2}$, &c.]. Few cuprous salts except those derived from haloid acids are known; a few double salts of this class have been prepared, *e.g.* $Cu_2SO_3.(NH_4)_2SO_3$, and some *cupro-cupric* salts are known, *e.g.* $Cu_2SO_3.CuSO_3.5H_2O$. The cuprous salts are generally insol. water, while the normal cupric salts as a class dissolve in water. The cuprous salts are less stable than the cupric; but cuprous iodide is so much more stable than cupric iodide, that the latter has not been isolated, reactions which might be expected to yield CuI_2

(*e.g.* KIAq + $CuSO_4Aq$) produce Cu_2I_2 and iodine. Many basic cupric salts are known. The cuprous salts are not generally obtained by reacting on Cu_2O with acids, but by reduction of cupric salts (*v. e.g.* CUPROUS CHLORIDE). Cupric salts are usually obtained by reactions between acids and CuO or $CuCO_3$. A great many cupric salts have been prepared (*v.* CARBONATES, NITRATES, SULPHATES, &c.); the following are the chief salts of this class:—*bromate*, *carbonates*, *chlorate* (and salts of other chlorine oxyacids), *iodate* and *periodate*, *molybdates*, *nitrates* and *nitrites*, *phosphate* (and salts of other phosphorus oxyacids), *selenates* and *selenite*, *silicates*, *sulphates* and *sulphites*, *tungstates*, *uranates*, *vanadates*.

Copper, selenides of. I. CUPROUS SELENIDE Cu_2Se. A steel-grey mass, obtained by heating Cu turnings with Se. Occurs native as *Berzelianite*. II. CUPRIC SELENIDE CuSe. A greenish-black solid, obtained by passing Se vapour over copper plates (Little, *A.* 112, 211); S.G. 6·66. Also formed by passing H_2Se into a solution of a cupric salt (Berzelius).

Copper, silicide of. No definite compound has been isolated. Bodies more or less resembling alloys of Cu and Si are obtained by heating K_2SiF_6 with Na and Cu (*v.* Deville a. Caron, *C. R.* 45, 163; Winkler, *J. pr.* 91, 193).

Copper, silicofluoride of, $CuSiF_6.6H_2O$. Blue crystals, obtained by dissolving CuO in H_2SiF_6Aq; deliquescent; heated to 60° gives $CuSiF_6.4H_2O$ (Berzelius; Stolba, *J. pr.* 102, 7). Decomposed at 130°-140° giving CuF.OH, SiF_4, and HF; absorbs NH_3 giving $CuF.OH.2NH_3$, NH_4F, and SiO_2 (Balbiano, *G.* 14, 74).

Copper, sulphides of. Two sulphides of copper are known, Cu_2S and CuS. As neither has been gasified the molecular formulæ are not known with certainty; Pickering (*C. J.* 39, 401) says that CuS heated in H at 260° gives Cu_2S, and at c. 650° it yields Cu; because of this reaction he thinks that the formula of cupric sulphide ought to be Cu_2S_2 and not CuS. *Cuprous sulphide*, Cu_2S, is the more stable of the two sulphides; both are distinctly basic, forming the basic radicles of various sulpho-salts; but CuS also combines with Na_2S &c., forming compounds in which CuS acts as the negative radicle (*v.* CUPROUS, and CUPRIC, SULPHIDE; *Combinations*). Compounds are also known which probably contain the radicle CuS_3 (*v.* p. 262).

I. CUPROUS SULPHIDE Cu_2S. Occurs native as *Copper-glance*; S.G. 5·97 (Karsten, *S.* 65, 320, 394). Crystallises in rhombic forms $a:b:c = \cdot582:1:\cdot973$; and also in regular octahedra; isomorphous in both forms with Ag_2S. Forms compounds with some less positive sulphides (*v. Combinations*).

Formation.—1. By heating a mixture of 4 parts finely divided Cu with 1 part S (Winkelblech, *A.* 21, 34). Spirals of Cu burn in S vapour to Cu_2S. Cu_2S is also formed by repeatedly and strongly pressing together a mixture of Cu and S (Spring, *B.* 16, 999).—2. By the action of NH_4SHAq on Cu (Heumann, *B.* 6, 748).—3. By heating $CuSO_4$ with carbon.

Preparation.—1. By heating electrolytically deposited copper with conc. H_2SO_4 for a short time at c. 124° (Pickering, *C. J.* 39, 402).—2. By heating pure CuS in a stream of H to c. 265° so long as H_2S is evolved (P., *l.c.*).—3. By passing H_2S into solution of a Cu salt in presence of $NaHCO_3$ at 200° (de Senarmont, *A. Ch.* [3] 32, 116).—4. By heating $CuSO_4$, or other Cu salt, in dry H_2S and then in H (Carnot, *Bl.* [2] 32, 163).

Properties and Reactions.—(S.G. *v. supra.*) Greyish-blue solid, fusible at moderate temperature.—1. Generally said to be unchanged when heated in *hydrogen*, but according to Pickering it is reduced to Cu by heating in H stream at c. 650° (*C. J.* 39, 404).—2. Reduced to Cu by heating to white heat in *water vapour* (Regnault, *A. Ch.* 62, 387).—3. *Chlorine* slowly acts on hot Cu_2S.—4. Heated in *air* gives $CuSO_4$ and CuO.—5. Heated with *cupric oxide* forms SO_2 and Cu or Cu_2O.—6. Heated with *litharge*, SO_2, a little Cu_2O, PbO, and Pb are formed.—7. *Phosphoretted hydrogen* forms Cu phosphide.—8. *Alkali carbonate* does not react with Cu_2S when the two are heated together, but in presence of carbon or caustic alkali a part of the Cu_2S is reduced to Cu.—9. Heated with *nitre*, K_2SO_4 and Cu are formed.—10. *Silver nitrate* reacts in accordance with the equation $Cu_2S + 4AgNO_3 = 2Cu(NO_3)_2 + Ag_2S + 2Ag$ (Heumann, *B.* 6, 751; 8, 534; Schneider, *P.* 152, 471; 154, 295).—11. Boiling conc. *hydrochloric acid* slowly forms Cu_2Cl_2; *cold nitric acid* forms CuS and $Cu(NO_3)_2$; *hot nitric acid* forms $Cu(NO_3)_2$ and separates S.—12. Heated in *carbon dioxide* to about 250°-300° Cu is formed (Pickering, *C. J.* 39, 405).

Combinations.—1. With *non-metallic sulphides* (i.) $Cu_2S.P_2S_3$, and $2Cu_2S.P_2S$; produced, the former by adding P_2S to ammoniacal Cu_2Cl_2Aq, the latter by heating the first to redness in a retort (Berzelius, *P.* 7, 29). (ii.) $2Cu_2S.P_2S_4$; the pp. from ammoniacal Cu_2Cl_2Aq by alkaline polysulphides is heated with P_2S (Berzelius). (iii.) $3Cu_2S.2As_2S_3$, occurs native as *Binnite*; $3Cu_2S.As_2S_5$ occurs native as *Enargite*. (iv.) $Cu_2S.Sb_2S_3$ occurs native as *Copper-antimony glance*; $3Cu_2S.Sb_2S_5$ is formed by heating $2Cu_2S.CuS.Sb_2S_5$ which is produced by precipitating $CuSO_4Aq$ by Na_3SbS_4.—2. With *metallic sulphides*. $Cu_2S.Fe_2S_3$, $3Cu_2S.Fe_2S_3$, and $Cu_2S.2FeS.Fe_2S_3$ occur as minerals. 3. *With non-metallic and metallic sulphides.* (i.) $4(Cu_2Fe)S.As_2S_3$ = *Tennantite*; $3Cu_2S\ 3FeS.As_2S_5$ = *Epigenite*. (ii.) $Cu_2S.2PbS.Sb_2S_3$ = *Bournonite*.

II. CUPRIC SULPHIDE CuS (or Cu_2S_2, *v.* beginning of COPPER, SULPHIDES OF) occurs native as *Covellite*; S.G. 4·59 to 4·64 (Karsten, *S.* 65, 320, 394). A green-black solid; by compressing at 6500 atmos. appears as dark-blue metal-like mass (Spring, *B.* 16, 1142). Acts as a basic sulphide, forming compounds with less positive sulphides; but also forms compounds with Na_2S &c., in which CuS forms the negative part of the salt.

Colloidal form of CuS (Spring a. De Boeck, *Bl.* [2] 48, 165). An aqueous solution of CuS is obtained by ppg. a Cu salt solution by H_2S, or preferably by NH_4HSAq, and prolonged washing by decantation with dilute H_2SO_4Aq, then dissolving in water and boiling for a few moments to expel H_2S. The aqueous solution of CuS is dark-coloured, with slight greenish fluorescence; the CuS is ppd. by addition of various salts, *e.g.* alum, Al_23SO_4, &c.

Formation. By adding an alkaline sulphide to solution of a Cu salt; Thomsen (*B.* 11, 2043) says that the pp. formed by adding Na_2SAq to

$CuSO_4Aq$ has the composition Cu_4S_3. By passing H_2S into solution of a Cu salt.

Preparation.—1. $CuSO_4Aq$, prepared from pure electrolytic Cu, is ppd. by H_2S, and the pp. is dried at a low temperature in a current of H_2S. 2. Pure electrolytic Cu is heated with conc. H_2SO_4 to about 180° for some little time, the residue is washed, and heated for a short time in a rapid current of H at c. 160° (Pickering, *C. J.* 39, 401).—3. Pure finely-divided Cu_2S is treated with cold conc. nitric acid, the residue is thoroughly washed.—4. $2\frac{1}{2}$ parts finely divided Cu (ppd. by Zn) are gently heated with $1\frac{1}{2}$ part flowers of S, so that the excess of S sublimes; any residual S may be removed by washing with KOHAq.

Properties and Reactions.—1. Moist CuS readily oxidises in *air* to $CuSO_4$.—2. *Heated* to c. 330° for some hours, Cu_2S is formed (Pickering, *C. J.* 39, 406).—3. Heated in *carbon dioxide* to c. 130° Cu_2S is formed, and at c. 350° Cu is produced; heated in *hydrogen* to c. 200° reduction begins, and at c. 265° Cu_2S is formed, and at c. 620° Cu is produced (Pickering, *C. J.* 39, 403). 4. Dissolved by *nitric acid* with separation of S, hot conc. *hydrochloric acid* slowly forms Cu_2Cl_2.—5. Dissolved by *potassium cyanide solution*, also by solution of *alkali bicarbonates*. 6. Insoluble in *alkali sulphides*.—7. Not attacked by H_2SO_4Aq containing $\frac{1}{6}$ of its volume of H_2SO_4 (Hofmann, *A.* 115, 286).

Combinations.—1. The following compounds of CuS with sulphide of arsenic and antimony are described by Berzelius, obtained by reactions between Cu salts and sulpharsenates and sulphantimonates (*P.* 7, 29); $2CuS.As_2S_5$; $12CuS.As_2S_3$; $2CuS.As_2S_3$; $3CuS.Sb_2S_5$.—2. Berzelius also describes the compounds with *phosphorus sulphides*, $CuS.P_2S$; $2CuS.P_2S_5$.—3. With *sulphides of the alkali metals*. Schneider (*P.* 138, 311) obtained $K_2S.3Cu_2S.2CuS$ ($=K_2Cu_8S_6$) by heating together 1 part finely-divided Cu, 6 parts K_2CO_3, and 6 parts S; when the same proportions of Cu, Na_2CO_3, and S were used, the compound $Na_2S.Cu_2S.CuS$ ($=Na_2Cu_4S_3$) was produced. Schneider also describes the compounds $K_2FeCu_4S_4$ and $Na_2FeCu_4S_4$, obtained by heating Fe, S, and K_2CO_3 or Na_2CO_3.

III. Compounds of hypothetical copper trisulphide (CuS_3). When $CuSO_4Aq$ to which excess of NH_3Aq has been added is dropped into $(NH_4)_2SAq$ until a pp. forms, the liquid is filtered and allowed to stand in absence of air, a salt $Cu_2(NH_4)_2S_7$ [$? = (NH_4)_2S.2CuS_3$] is formed in red needles. This compound is decomposed on exposure to air, or by addition of warm water. A corresponding K salt was obtained by Priwoznik (*B.* 6, 1291) by the action of alkali polysulphides on Cu_2O, CuO, or Cu_2S. (For more details *v.* Priwoznik, *l.c.*; Peltzer, *A.* 128, 184; Gescher, *A.* 141, 350; 143, 375; Bloxam, *C. J.* [2] 3, 94; Vohl, *J. pr.* 102, 32; Berzelius, *P.* 7, 29).

Copper, telluride of. By boiling a solution of Cu acetate in presence of ppd. Te, Parkman (*J.* 1861. 126) obtained Cu_2Te_4 as a black powder. If the solution is cold and SO_2 is added, the pp. is CuTe. M. M. P. M.

COPPER-AMMONIUM COMPOUNDS. (*Cuprammonium compounds. Cupramines*). Many of the bodies which are formed by the combination of NH_3 with the haloid and other compounds of Cu may be regarded as compounds of various hypothetical radicles supposed to be derived from NH_4, N_2H_8, N_3H_{12}, &c., by replacing H_2 by Cu_2 or Cu. Thus the compounds $CuCl_2.2NH_3$ and $Cu_2Cl_2.2NH_3$ may be formulated as $N_2H_6(Cu)Cl_2$ and $N_2H_6(Cu_2)Cl_2$ respectively. From these compounds others may be derived by assuming that part of the H is substituted by NH_4; thus the compound $CuCl_2.4NH_3$ may be formulated as $N_2H_4(NH_4)_2(Cu)Cl_2$. Compounds supposed to be derived from the hypothetical radicle $N_2H_6(Cu_2)$ are sometimes called *cupro-ammonium compounds*; examples of these are *cupro-ammonium chloride* $N_2H_6(Cu_2)Cl_2$, *diammonium-cupro-ammonium iodide* $N_2H_4(NH_4)_2(Cu_2)I_2$. Compounds supposed to be derived from the hypothetical radicle $N_2H_6(Cu)$ are sometimes called *cupri-ammonium compounds*; examples of these are *cupri-ammonium chloride* $N_2H_6(Cu)Cl_2$, *diammonium-cupri-ammonium oxide* $N_2H_4(NH_4)_2(Cu)O$. It is, however, very doubtful whether anything is gained at present by this extremely hypothetical way of formulating the double compounds of NH_3 and Cu salts. M. M. P. M.

COPRINE. A name given by Niemikowicz (*M.* 7, 241) to the methylo-hydroxide of Dimethyl-amido-acetone (*q. v.*).

COPTINE. An alkaloid contained, together with berberine, in *Coptis trifolia* (Gross, *N. Rep. Pharm.* 23, 53; Schultz, *Ph.* [3] 14, 973; *J. Ph.* 14, 273).

CORALLIN *v.* Rosolic acid and anhydride of Tri-oxy-di-phenyl-tolyl-carbinol.

CORIAMYRTIN $C_{30}H_{36}O_{10}$. [220°]. S. 1·44 at 22°. S. (alcohol) 2 at 22°. $[\alpha] = 24·5$ at 20°. The active principle of *Coriaria myrtifolia*, a purgative and poisonous plant growing in Southern Europe (Riban, *Bl.* 1864, i, 87; 1867, i, 79), formerly used for the production of a black dye. Prisms (from alcohol). Dextrorotatory III forms a black pp. which gives an alcoholic solution, which is turned crimson by NaOH. Baryta forms $BaC_{30}H_{16}O_{16}$(?). Br gives $C_{30}H_{34}Br_2O_{10}$, which crystallises in needles (from alcohol).

Hexa-acetyl derivative $C_{30}H_{30}Ac_6O_{10}$ 3aq [below 100°]. Transparent brittle mass.

CORIANDER OIL $C_{10}H_{17}OH$. $[\alpha]_D = -92·55°$ at 15°. The volatile oil of Coriander seeds (Trommsdorff, *Ar. Ph.* [2] 2, 114; Kawalier, *J. pr.* 58, 226). Decomposed by distillation forming $C_{20}H_{34}O$ (165°–170°). P_2O_5 forms a terpene $C_{10}H_{16}$. On treatment with iodine it gives cymene. It forms a solid sodium derivative $C_{10}H_{17}ONa$ and various ethers. On oxidation with neutral $KMnO_4$ it gives a ketone $C_{10}H_{16}O$ (186°), S.G. ·897, which combines with $NaHSO_3$, and is converted by further oxidation into CO_2, acetic acid, and dimethyl-succinic acid. Alkaline $KMnO_4$ oxidises it to CO_2, acetic, and oxalic acids (Grosser, *B.* 14, 2185). HCl forms $C_{10}H_{17}Cl$, S.G. ·953, while HI gives $C_{10}H_{17}I$, which explodes below 100°.

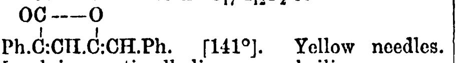
CORIDINE $C_{10}H_{15}N$. (211°). S.G. ^{22} ·974. A base of the pyridine series occurring in coal tar (Thenius, *C. C.* 1862, 53). Turns litmus paper blue. Sl. sol. water, v. sol. other ordinary menstrua. The hydrochloric acid solution gives a pp. with $HgCl_2$, which melts at 28°, but may be obtained as white needles. Colours acidified pine wood yellowish red.—$B'_2H_2PtCl_6$: orange pp.

CORK *v.* Cellulose, vol. i. p. 721.

CORNEÏN *v.* PROTEÏDS, *Appendix C.*

CORNICULARIC ACID $C_{17}H_{14}O_3$ or $Ph.C(CO_2H):CH.CO.CH_2.Ph.$ [115°]. Long colourless needles or tables. Formed as a by-product in the reduction of pulvic acid to di-hydro-cornicularic acid. This latter acid is also formed by reduction of cornicularic acid with zinc-dust and NaOH (Spiegel, *B.* 15, 1546; *A.* 219, 23).

Cornicular-lactone $C_{17}H_{12}O_2$ or



$$\begin{array}{l} OC\text{---}O \\ \;\;|\qquad\;\;| \\ Ph.C:CH.C:CH.Ph. \end{array}$$

[141°]. Yellow needles. Insol. in caustic alkalis even on boiling.

Di-hydro-cornicularic acid $C_{17}H_{16}O_3$ *i.e.* $(C_6H_5)_2C_4H_4(OH).CO_2H$. *Di-phenyl-oxy-angelic acid.* [134°]. Colourless needles. Sol. alcohol, ether, benzene, and acetic acid, sl. sol. CS_2, insol. ligroin. Prepared by reduction of pulvic acid with zinc-dust and NH_3, CO_2 being evolved. On further reduction with sodium amalgam it gives tetra-hydro-cornicularic acid. On fusion with KOH it is resolved into phenyl-succinic acid and toluene. Distillation with quick-lime gives $C_6H_5.CH_2.CH_2.CO.CH_2.C_6H_5$. Ac_2O forms a compound $C_{17}H_{14}O_2HOAc$ [99°].

Salts.—A′Ag and A'_2Pb: amorphous white pps.

Methyl ether A′Me: colourless monoclinic prisms [68°], formed by reduction of pulvic ether or from silver dihydrocornicularate and EtI.

Lactone $C_{17}H_{14}O_2$. [117°]. Colourless needles. Sol. ether, benzene, acetic acid, hot alcohol, and CS_2, slightly in ligroin. Prepared by heating the acid (Spiegel, *B.* 14, 1690).

Tetra-hydro-cornicularic acid $C_{17}H_{18}O_3$ or $C_6H_5.CH_2.CH(OH).CH_2CH(C_6H_5).CO_2H$(?). *Di-phenyl-oxy-valeric acid.* Thick colourless oil. Formed by reduction of di-hydro-cornicularic acid with sodium amalgam (Spiegel, *B.* 14, 1692).

Lactone $C_{17}H_{16}O_2$. [71°]. Flat colourless needles. Sol. alcohol, ether, and benzene, sl. sol. ligroin, insol. water. Formed by boiling the acid with water (Spiegel, *B.* 14, 1692).

Iso-**Di-hydro-cornicular-lactone** $C_{17}H_{14}O_2$. [c. 105°]. Colourless needles. Formed as a by-product in the reduction of pulvic acid (Spiegel, *B.* 15, 1546).

CORNIN. A crystalline bitter substance which may be extracted by water from the root of *Cornus florida* (Geiger, *A.* 14, 206). Ppd. by lead subacetate.

CORTICIC ACID $C_{12}H_{10}O_6$? An amorphous acid said to exist in cork (Siewert, *Z.* 1868, 383).

CORYDALINE $C_{18}H_{19}NO_4$. [130°]. Occurs in the roots of *Corydalis bulbosa*, *C. fabacea*, and *Aristolochia cava* (Wackenroder, *Kastn. Arch.* (1826); Peschier, *Trommsd. N J.* 17, 80; Winckler *Pharm. Centr.* 1832, 38; *A.* 87, 225; Ruickholdt, *A.* 64, 369; Muller, *Vierteljahr. pr. Pharm.* 8, 526; Wicke, *A.* 137, 274). The alkaloid is extracted by dilute acid, and may be isolated after ppn. by sodium phosphotungstate. Short prisms (from strong solutions) or slender needles (from dilute solutions); insol. water, sol. ordinary solvents. Tastes bitter. Ppd. by NaOH from its solution in acids, the pp. being sol. excess. Ppd. by the usual reagents for alkaloids.—B′HCl 5aq: tufts of needles.—$B'_2H_2PtCl_6$: yellow crystalline pp.—$B'H_2SO_4$: needles, sl. sol. water.

Ethylo-iodide B′EtI. Crystalline, sl. sol. water. Not decomposed by aqueous NaOH, but converted by moist Ag_2O into an alkaline hydroxide.—$(B'EtCl)_2PtCl_4$: amorphous pp.

COTARNAMIC ACID *v.* NARCOTINE.

COTARNIC ACID *v.* NARCOTINE.

COTARNINE *v.* NARCOTINE.

COTO BARK. Two kinds of coto bark are exported from Bolivia, one from the interior of the country called cinchona-coto or genuine coto, derived probably from some plant belonging to the Lauraceæ or Terebinthaceæ, rather than to the Rubiaceæ. It is used in cases of diarrhœa and colic, as also for neuralgia, rheumatism and gout. The other kind of coto-bark or paracoto-bark (Jobst a. Hesse), from the banks of the river Mapiri, resembles the former in appearance, though its physiological action is much weaker. True coto bark contains cotoin and dicotoin; the other bark contains paracotoin, hydrocotone, and its dibenzoyl derivative, leucotin, and oxyleucotin; piperonylic acid is present in both (Harz, *Ar. Ph.* [3] 7, 214; Gietl, *ibid.* 221; Wittstein, *ibid.* 219; Burkart, *Med. Corres. Artz. Verein Würtemburg*, 1876; Balz, *Centralblatt Med. Wiss.* 1878; Jobst a. Hesse, *A.* 199, 17). The physiological action of cotoin and paracotoin has been studied by Albertoni (*J.* 1883, 1353, 1488).

Cotoin $C_{22}H_{18}O_6$. [130°].

Preparation. The finely-powdered coto-bark is exhausted with ether, the extract evaporated to one-tenth, and the residue mixed with warm petroleum; on cooling a black resinous mass separates, the liquid from which on evaporation deposits crystals of cotoin. From the resin the compound is also obtained by boiling with lime, and the solution acidified with acetic acid; from this liquid cotoin is deposited in leaflets or pale golden needles. It is finally purified by charcoal.

Properties.—Prisms or tabular crystals, v. sol. alcohol, chloroform, and benzene, sl. sol. water and petroleum; sol. alkalis and their carbonates, but reprecipitated on acidification. Neutral to litmus. Inactive.

Reactions.—1. With *nitric acid* it gives a blood-red colouration.—2. *Reduces* gold and silver salts and Fehling's solution when warmed.—3. With *ammonia* and $Pb(OAc)_2$ it gives a yellow flocculent pp. $C_{22}H_{12}Pb_3O_6$.—4. Heated with concentrated *acids* or *alkalis* it yields benzoic acid.

Triacetyl derivative $C_{22}H_{15}Ac_3O_6$. [94°]. Prisms, sol. $CHCl_3$ and water.

Tri-bromo-cotoin. [114°]. Yellow prisms, insol. cold water, decomposed by hot water, sol. alcohol, chloroform, and ether.

Dicotoïn $C_{44}H_{34}O_{11}$. *Anhydride of cotoïn?* [74°–77°]. When crude cotoin is treated with boiling water, crystals of cotoin at first separate, then leaflets of dicotoin, which are separated by a sieve. Pale-yellow glistening leaflets, sol. alcohol, acetone, ether, and alkalis. By potash it is converted into cotoin; and by Ac_2O into tri-acetyl-cotoin (Jobst a. Hesse, *A.* 199, 29).

Paracotoin $C_{19}H_{12}O_6$. [152°].

Preparation.—Finely divided para-coto bark is extracted with ether, and from the residue left on evaporation a crystalline mass of paracotoin, oxyleucotin, leucotin, and its di-benzoyl derivative separates out. This is fractionally crystallised from alcohol, when the paracotoin separates out first.

Properties.- Pale yellow leaflets, sol. ether and chloroform; of neutral reaction; does not react with Ac_2O.

Reactions.—1. Sol. *nitric acid* forming a yellow nitro- product. 2. Br gives an unstable bromo- derivative. 3. On fusion with *potash* it yields formic and protocatechuic acids, but when boiled with a solution of *potash* paracumarhydrin is formed thus $C_{19}H_{12}O_6 + 2H_2O = 2C_9H_8O_3 + CO_2$ together with paracotoic acid.

Hydrocotoin $C_{15}H_{14}O_4$. [98°]. Occurs in para-coto bark. Extracted by dilute soda from the resinous mass obtained after separation of the paracotoin, leucotin, and oxyleucotin. Large pale yellow prisms, sol. hot water and alcohol, v. sol. chloroform and acetone. With *ferric chloride* and *sulphuric acid* it gives a dark-brown colouration; with *bromine* it gives a bromo- derivative $C_{15}H_{13}BrO_4$, crystallising in monoclinic prisms [147°], sol. ether, chloroform, and alcohol. Further bromination gives a di-bromo- derivative, $C_{15}H_{12}Br_2O_4$, crystallising in prisms [95°]. On fusion with potash it yields hydrocotone and benzoic acid (Jobst a. Hesse, *A.* 199, 57).

Acetyl derivative $C_{15}H_{13}O_3(OAc)$. [83°]. White prisms. V. sol. hot water. Forms a bromo- derivative $C_{15}H_{12}BrAcO_4$, [166°], crystallising in white prisms, sol. chloroform and boiling alcohol.

Hydrocotone $C_{18}H_{24}O_6$. [49°]. (243°). V.D. 11·16. Formed by fusion of leucotin with potash; white prisms, sol. ether, acetone, and chloroform. Heated with concentrated nitric acid it yields di-nitro-cotone $C_{18}H_{20}(NO_2)_2O_6$, which crystallises in brown leaflets of metallic lustre; when heated it explodes, emitting violet vapours.

Di-benzoyl- derivative $C_{18}H_{22}Bz_2O_6$. [113°]. Occurs in the para-coto bark; white prisms, sol. alcohol, ether, and acetone, sl. sol. hot water. Concentrated *nitric acid* forms with it a bluish-green resin. *Sulphuric acid* gives a dark-yellow colouration. On fusion with *potash* it yields hydrocotone and benzoic acid. It is unaltered by acetic anhydride. With *bromine* it yields a di-bromo- derivative $C_{32}H_{30}Br_2O_8$ [147°], crystallising in white prisms, sol. alcohol and acetone, as well as a tetra-bromo- derivative $C_{32}H_{28}Br_4O_8$ [84°], crystallising in octahedra, sol. alcohol and chloroform.

Paracumarhydrin $C_9H_8O_3$. [83°]. Formed by boiling paracotoin with aqueous KOH. Laminæ; smelling like coumarin; sl. sol. cold water, v. e. sol. alcohol.

Leucotin $C_{10}H_{31}O_2$. [97°]. The chief constituent of the extract of para-coto bark. Separates from the alcoholic mother-liquor in the preparation of para-cotoin. Small prisms. Sl. sol. boiling water, v. sol. alcohol and ether. Inactive. Not attacked by Ac_2O. HNO_3 gives a bluish-green resin and solution. Potash-fusion gives benzoic, formic, and protocatechuic acids, protocatechuic aldehyde, cotogenin, and hydrocotoin. Br gives a di-bromo- derivative $C_{34}H_{30}Br_2O_2$ [187°], and a tri-bromo- derivative $C_{34}H_{29}Br_3O_2$ [157°].

Cotogenin $C_{14}H_{11}O_5$. [210°]. Obtained by fusing leucotin with KOH. May be crystallised from HOAc. Gives off pyrocatechin when strongly heated. V. sl. sol. cold alcohol and ether. Dissolves in alkalis, forming solutions which turn brown in the air. Fe_2Cl_6 colours its alcoholic solution green.

Paracotoïc acid $C_{19}H_{14}O_7$. [108°]. Formed by boiling paracotoin with dilute alkalis $C_{19}H_{12}O_6 + H_2O = C_{19}H_{14}O_7$. Yellow amorphous powder, sol. alcohol and ether, insol. water. The Ba, Pb, and Ca salts (MA'_2) are yellow amorphous pps.

Oxyleucotin $C_{34}H_{32}O_{12}$. [134°]. Occurs in paracoto bark. Prisms (from alcohol). V. e. sol. alcohol and HOAc, m. sol. ether. By heating with conc. HNO_3 it is converted into a bluish-green resin and a bluish-green solution. Inactive. It is not coloured by Fe_2Cl_6. Conc. HCl at 140° gives protocatechuic acid. Potash-fusion gives protocatechuic acid and aldehyde, benzoic acid, formic acid, and cotogenin. Br gives a di-bromo- derivative $C_{34}H_{30}Br_2O_{12}$ [192°], and a tetra-bromo- derivative $C_{34}H_{28}Br_4O_{12}$ [159°].

PARACOTO OIL. Prepared from the para-coto bark by distillation with superheated steam. Light mobile liquid. S.G. $^{\underline{15}}$ ·93, $\alpha = -2{\cdot}12$; separated by fractional distillation into (α) and (β) paracotene, (α), (β) and (γ) paracotole.

(α) **Paracotene** $C_{12}H_{18}$. V.D. 5·17. (160°). S.G. $^{\underline{15}}$ ·87. $[\alpha]_D = +9{\cdot}34$. Strongly refractive oil of aromatic odour.

(β) **Paracotene** $C_{11}H_{18}$. (171°). V.D. 4·83. S.G. $^{\underline{15}}$ ·88. $[\alpha]_D = -{\cdot}63$. Oil, of faint aromatic odour.

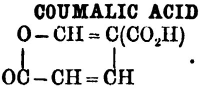
(α) **Paracotole** $C_{15}H_{24}O$. (221°). V.D. 6·17. S.G. $^{\underline{15}}$ ·93. $[\alpha]_D = -11{\cdot}87$, isomeric with the oil of cubebs, which it resembles in many respects.

(β) **Paracotole** $C_{28}H_{10}O_2$. (236°). V.D. 12·8. S.G. $^{\underline{15}}$ ·95. $[\alpha]_D = -5{\cdot}98$. Oil of faint aromatic odour.

(γ) **Paracotole** $C_{28}H_{10}O_2$. (240°). S.G. $^{\underline{15}}$ ·97. $[\alpha]_D = -{\cdot}52$. Turns yellow on exposure from absorption of oxygen (Jobst a. Hesse, *A.* 199, 75).

COTTON *v.* CELLULOSE.

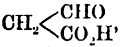
COUMALIC ACID $C_6H_4O_4$ *i.e.*



$$\begin{matrix} O-CH=C(CO_2H) \\ | \qquad\qquad | \\ OC-CH=CH \end{matrix}$$

. *Cumalic acid.* [207°]

Prepared by heating malic acid with H_2SO_4 or $ZnCl_2$, and precipitating the melt in water; the yield is nearly theoretical. The reaction probably consists in the splitting off of formic acid with production of the semi-aldehyde of malonic acid



$CH_2\!<\!\begin{matrix}CHO\\ CO_2H\end{matrix}$, which then undergoes further condensation, forming coumalic acid (Pechmann, *B.* 17, 936). Sublimable. Small colourless prisms. V. sol. alcohol and acetic acid, sl. sol. cold, more sol. hot, water. It reduces ammoniacal silver and copper solutions on boiling. Its aqueous solution is decomposed on boiling. On oxidation it gives fumaric acid. NH_3 forms, in the cold, oxy-pyridine carboxylic acid.

Methyl ether A'Me: [74°]; (c. 260°), long, colourless needles or plates.

Coumal-anilidic acid
$CO_2H.CH:CH.C(CO_2H):CH.NHPh.$ (?)

Mono-methyl ether
$CO_2H.CH:CH.C(CO_2Me):CH.NHPh.$ [140°].

Formed by the action of aniline on an alcoholic solution of the methyl-ether of coumalic acid (Pechmann a. Welsh, *B.* 17, 2392; *C. J.* 47, 145). Yellow needles, v. sol. hot alcohol, chloroform, and benzene, sl. sol. ether, insol. water. By boiling with aqueous NaOH it is converted into the phenyl derivative of oxy-nicotinic acid—$C_5H_3N(OPh)CO_2H$[1:2:5].

Bromocoumalic acid *v.* vol. i. p. 565.

PARACOUMARHYDRIN *v.* Coto bark.

o-**COUMARIC ACID** $C_9H_8O_3$. *o-Oxy-cinnamic acid. o-Oxy-phenyl-acrylic acid.* Mol. w. 164. [208°]. V.D. 6·5 (calc. 6·66).

Occurrence.—In melilot (*Melilotus officinalis*) and in the leaves of *Angræcum fragrans* (Zwenger, *A. Suppl.* 8, 30).

Formation.—From *o*-amido-cinnamic acid by the diazo- reaction (Fischer, *B.* 14, 479; *A.* 221, 274).

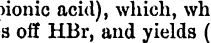
Preparation.—Coumarin (10 g.) is added to a solution of sodium (3·5 g.) in dry alcohol (65 c.c.), and the mixture heated for 1½ hours. The product is diluted and evaporated to a small bulk. The coumaric acid is ppd. by HCl. The pp. is dissolved in Na_2CO_3Aq, freed from unaltered coumarin by shaking with ether, the acid is reppd. by HCl and crystallised from water (Ebert, *A.* 226, 347; *cf.* Delalande, *A. Ch.* [3] 6, 343; *A.* 45, 333; Bleibtreu, *A.* 59, 183).

Properties.—Long needles, v. sl. sol. cold water and ether, v. sol. alcohol, insol. $CHCl_3$ and CS_2. Not volatile with steam. Decomposed on distillation with formation of phenol. Its solution in alkalis is yellow with green fluorescence. Conc. HBrAq slowly changes it in the cold into its anhydride, coumarin.

Reactions.—1. *Potash-fusion* gives acetic and *o*-oxy-benzoic acids.—2. *Sodium amalgam* gives *o*-oxy-phenyl-propionic acid (Tiemann a. Herzfeld, *B.* 10, 286).—3. *Bromine* (1 mol.) added to its solution in CS_2 gives a white crystalline substance [c. 111°] (? di-bromo-*o*-oxy-phenyl-propionic acid), which, when exposed to the air, gives off HBr, and yields (β)-di-bromo-coumarin [177°].

Salts.—BaA'_2 aq: nodules, v. sol. water.—PbA'_2: crystalline pp.—ZnA'_2: needles, sl. sol. cold water.—AgA′.

Constitution.—Like cinnamic, fumaric, and citraconic acids, coumaric acid is a symmetrical derivative of ethylene, so that it might be expected to exist in two modifications. These two modifications are found in its alkyl derivatives. The existence of two modifications might also be accounted for by ascribing to one of them the formula



$C_6H_4\left<\begin{array}{l}CH{:}CH\\ \quad\;\;|\\ O.\;\;C(OH)_2\end{array}\right.$

(Anschutz, *A.* 239, 161; 240, 133). Except as regards boiling-point, the physical properties of the (α)-coumaric ethers stand to those of their (β)-isomerides exactly as those of citraconic and maleic ethers stand to those of mesaconic and fumaric ethers respectively (Perkin, *C. J.* 39, 559).

(α)- (or *Allo-*) *Methyl derivative* $C_6H_4(OMe).CH{:}CH.CO_2H$. [89°]. Formed by heating coumarin with NaOH (2 mols.) and MeI (1 mol.) at 150° (Perkin, *C. J.* 39, 409). Monoclinic crystals (from CS_2). *a*:*b*:*c* = ·677:1:1·122; β = 87° 12′. V. e. sol. alcohol, m. sol. ligroïn. Changes into the (β)-isomeride on boiling, or even by exposing a concentrated alcoholic solution to sunlight. Sodium amalgam reduces it, as well as its (β)-isomeride, to the methyl derivative of oxy-phenyl-propionic acid. Br in CS_2 gives the methyl ether of (α)-di-bromo-*o*-oxy-(β)-phenyl-propionic acid (*v.* vol. i. p. 603). Undiluted bromine forms the methyl-ether of tri-bromo-oxy-phenyl-propionic acid. HNO_3 gives the same di-nitro- derivative as with its (β)-isomeride. Fuming HI unites in the cold, and on adding Na_2CO_3 there is formed $C_6H_4(OMe)CH{:}CH_2$. $KMnO_4$ oxidises it to [2:1] $C_6H_4(OMe)CO_2H$. — BaA'_2. — Methyl ether [2:1]$C_6H_4(OMe).CH{:}CH.CO_2Me$. (276°). S.G. $\frac{15}{15}$ 1·140; $\frac{30}{30}$ 1·278. Formed by heating coumarin, MeOH, and MeI for 3 hours at 100°. Converted by NH_3 at 150° into the amide of the (β)-isomeride.

(β)-*Methyl derivative* [2:1]$C_6H_4(OMe).CH{:}CH.CO_2H$. [183°]. Formed by heating [2:1]$C_6H_4(OMe).CHO$ (2 pts.) with NaOAc (1 pt.) and Ac_2O (3 pts.) at 175° (Perkin, *C. J.* 31, 411). Formed also by heating its (α)-isomeride. Small monoclinic prisms (from xylene) *a*:*b*:*c* = ·141·1:·807; β = 64° 41′. M sol. alcohol. Br in CS_2 gives the methyl derivative of (β)-di-bromo-oxy-phenyl-propionic acid (*v.* vol. i. p. 603). Undiluted bromine forms the methyl ether of tri-bromo-oxy-phenyl-propionic acid. $KMnO_4$ gives $C_6H_4(OMe).CO_2H$ (Tiemann a. Will, *B.* 15, 2078). *Potash-fusion* gives salicylic acid. HNO_3 forms a di-nitro-derivative [193°].—Methyl ether $C_6H_4(OMe).CH{:}CH.CO_2Me$. [293°]. S.G. $\frac{15}{15}$ 1·1486; $\frac{30}{30}$ 1·1362. V.D. 6·5 (calc. 6 6). M.M. 2·389. μ_D 1·5905 at 10°. Obtained by means of PCl_5 and HOMe. Formed also by heating its (α)-isomeride. With Br in CS_2 it gives $C_6H_4(OMe).CHBrCHBr.CO_2Me$ [68°] and an isomeride [125°].

Amide $C_6H_4(OMe).CH{:}CH.CONH_2$. [192°]. Small needles (from alcohol).

(α)- (or *Allo-*) *Ethyl derivative* [2:1]$C_6H_4(OEt)CH{:}CH.CO_2H$. [102°] (F. a. E.); [104°] (P.). From alcohol, sodium (3·2 g.), coumarin (10 g.) and EtI (12 g.) (Fittig a. Ebert, *A.* 216, 142; Perkin, *C. J.* 39, 412). White plates (from water), or tables (from dilute alcohol). V. sl. sol. cold water, sl. sol. hot water, v. sol. alcohol and ether. Sparingly volatile with steam. *Reactions.*—1. On distillation an oil is got, whence Na_2CO_3 extracts the (β)-isomeride; the yield is 30 p.c.—2. $KMnO_4$ gives ethyl-salicylic aldehyde and acid.—3. Sodium amalgam forms the ethyl derivative of oxy-phenyl-propionic acid.—4. Br forms a dibromide [155°]. Salts.—$(C_{11}H_{11}O_3)_2Ba$ 2aq.—CaA'_2 2aq. S. 2 11 at 21°.

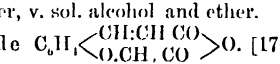
Ethyl ether $C_6H_4(OEt).CH{:}CH.CO_2Et$. (291°). S.G. $\frac{15}{15}$ 1·084; $\frac{30}{30}$ 1·074. μ_D = 1·558. From coumarin (14½ g.), NaOH (8 g.) and water, by evaporating to a small bulk and heating the residue with alcohol and EtI (32 g.) at 100°.

(β)-*Ethyl derivative* $C_6H_4(OEt)CH{:}CH.CO_2H$. [133°] (E. a. F.); [135°] (P.). Formed, together with the (α)-isomeride, by treating *o*-coumaric acid with NaOEt and EtI. Formed also from the (α)-isomeride by distillation, or by long heating to a high temperature (Fittig a. Ebert, *A.* 216, 144). Obtained by heating $C_6H_4(OEt)CHO$ with NaOAc and acetic anhydride at 160° (Perkin, *C. J.* 39, 413). Needles (from water), or prisms (from alcohol). V. sl.

sol. cold water, sl. sol. hot water. V. e. sol. alcohol or ether. The Na salt is oxidised by $KMnO_4$ to ethyl-salicylic aldehyde and ethyl-salicylic acid. Sodium amalgam forms the ethyl derivative of oxy-phenyl propionic acid. Br forms a dibromide [155°]. Salts.- $(C_{11}H_{11}O_3)_2Ca$ 2aq. S. ·43 at 21°. BaA'_2 4aq. Ethyl ether $C_6H_4(OEt).CH\,CH.CO_2Et$. (303°). S.G. $\frac{17}{17}$ 1·09. Formed by treating the preceding with PCl_5, followed by alcohol. Formed also by boiling the (α)-isomeride for some time.

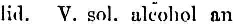
Acetyl derivative $C_6H_4(OAc).CH:CH.CO_2H$. [146°]. Formed by gently heating salicylic aldehyde (3 pts.) with NaOAc (4 pts.) and Ac_2O (5 pts.) (Tiemann a. Herzfeld, *B.* 10, 284). Needles (from water). V. sol. hot water, alcohol, and ether. Converted by dilute KOHAq into coumaric acid; and by heating above 150° into HOAc and coumarin.

Carboxy-methyl derivative $CO_2H.CH_2.O.C_6H_4.CH.CH.CO_2H$. *o-Coumar-oxy-acetic acid.* [190°]. Formed by heating o-aldehydo-phenoxy-acetic acid (1 pt.) with acetic anhydride (5 pts.) and sodium acetate (3 pts.) to boiling for 1 or 2 hours (Rossing, *B.* 17, 2997). Yellow needles. V. sol. alcohol, ether, and hot water, sl. sol. benzene, chloroform, and cold water. Sublimable.

Di-bromide 

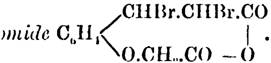
$C_6H_4<\begin{matrix}CHBr.CHBr.CO_2H\\O.CH_2.CO_2H\end{matrix}$.

[220°]. White needles; sl. sol. benzene, chloroform, and water, v. sol. alcohol and ether.

Anhydride 

$C_6H_4<\begin{matrix}CH:CH\,CO\\O.CH_2\,CO\end{matrix}>O$.

[176°]. Crystalline solid. V. sol. alcohol and ether, sl. sol. water. Formed by heating the acid with phosphoric acid.

Di-bromide 

$C_6H_4<\begin{matrix}CHBr.CHBr.CO\\ \quad\quad\quad\quad\quad\;|\\O.CH_2.CO\;-\;O\end{matrix}$.

[c.213°]. Orange-yellow needles; v. sol. alcohol and ether, sl. sol. water and benzene (Rossing, *B.* 17, 3001).

Bromo-coumaric acid *v.* vol. i. p. 564.

m-**Coumaric acid**

$[3:1]C_6H_4(OH).CH:CH.CO_2H$. [191°]. Formed by heating *m*-oxy-benzaldehyde with acetic anhydride and sodium acetate; or by boiling diazocinnamic acid with water (Tiemann a. Ludwig, *B.* 15, 2018). White prisms. Sol. alcohol, ether, benzene, and hot water.

Acetyl derivative $C_6H_4(OAc).CH:CH.CO_2H$. [151°]. White needles, sol. alcohol, ether, and hot water.

Methyl derivative $C_6H_4(OMe).CH:CH.CO_2H$. [115°]. Long white needles, sol. alcohol, ether, and benzene, sl. sol. hot water (Tiemann a. Ludwig, *B.* 15, 2018).

Carboxy-methyl derivative $C_{11}H_{10}O_5$ *i.e.* $C_6H_4(O.CH_2.CO_2H).CH:CH.CO_2H$ [1:3]. *m-Phenoxy-acetic-acrylic acid. m-Cumaroxy-acetic acid. Phenyl-glycollic-m-acrylic acid.* [219°]. Prepared by heating *m*-aldehydo-phenoxy-acetic acid with sodium acetate and acetic anhydride. White needles (from hot water). V. sol. alcohol, ether, and acetic acid, sl. sol. cold water. The Ag, Pb, Cu, and Fe salts are sparingly soluble pps. (Elkan, *B.* 19, 3047).

p-**Coumaric acid** $C_6H_4(OH).CH:CH.CO_2H$. *p-Oxy-cinnamic acid. p-Oxy-phenyl-acrylic acid. Naringenic acid.* [206°].

Preparation.—1. 2½ kilos. of aloes are boiled for two hours with 5 litres of water and 400 g. conc. H_2SO_4; after cooling the liquor is decanted and the residue again boiled with 2 litres of water, the combined extracts are evaporated to ⅓, and when cold extracted with ether. The crude *p*-coumaric acid (yield: 1·5 to 1·8 p.c.) left on evaporating the ether is purified by conversion into the barium salt (Hlasiwetz, *A.* 136, 31; Eigel, *B.* 20, 2527).—2. *p*-Oxy-benzaldehyde (5 pts.) is heated at 175° with dehydrated sodium acetate (8 pts.) and acetic anhydride (10 pts.); the yield is 70 p.c. of the oxy-benzaldehyde (Tiemann a. Herzfeld, *B.* 10, 63, 283; Eigel). 3. By heating *p*-diazo-cinnamic acid with water; small yield (Gabriel, *B.* 15, 2301).—4. Together with phloroglucin by boiling naringenin with conc. aqueous NaOH (Will, *B.* 20, 299).

Properties. Thick warts (anhy.) or long needles (with *x*aq). V. sl. sol. cold water, v. sol. hot water, v. e. sol. alcohol and ether, sl. sol. benzene, insol. ligroin. Fe_2Cl_6 colours the alcoholic solution brown. Sodium-amalgam gives *p*-oxy-phenyl-propionic acid. Potash-fusion forms *p*-oxy-benzoic acid (Barth, *B.* 12, 1259).

Salts.—NH_4A'aq· monoclinic tables.—CdA'_2 3aq.—CuA'_2 6aq.—AgA'.

Methyl derivative $C_6H_4(OMe).CH:CH.CO_2H$. [169°] (E); [171°] (P.). Formed by heating anisic aldehyde with acetic anhydride and sodium acetate at 180° (yield: 70 p.c. of the anisic aldehyde), or by saponification with KOH of the di-methyl-ether $C_6H_4(OMe).CH:CH.CO_2Me$ formed by heating the acid with methyl iodide and KOH. Occurs among the products of the action of KOH and MeI upon tyrosine (Korner a. Menozzi, *G.* 11, 519). Formed also by oxidising the methyl derivative of methyl oxy-styryl ketone with NaOCl (Einhorn a. Grabfield, *A.* 243, 363). Yellow needles, m. sol. alcohol, hot water, and HOAc; sl. sol. cold water and chloroform (Perkin). Gives when heated the methyl derivative of vinyl-phenol $CH_2:CH.C_6H_4OMe$. This body is also formed by successive treatment with HI and Na_2CO_3 (Perkin, *C. J.* 33, 214).—A'Na. — AgA' (Eigel, *B.* 20, 2527).

Methyl ether $C_6H_4(OMe).CH:CH.CO_2Me$. [89°]. (303°). Laminæ. In chloroform solution it takes up bromine, with production of $C_6H_4(OMe)CHBr.CHBr.CO_2Me$ [118°] (Valentini, *G.* 16, 424; Perkin, *C. J.* 39, 439).

Chloride $C_6H_4(OMe).CH:CH.COCl$. [50°].

Amide $C_6H_4(OMe).CH:CH.CONH_2$. [186°].

Acetyl derivative $C_6H_4(OAc).CH:CH.CO_2H$. [c. 195°]. Formed by heating sodium *p*-oxy-benzoic aldehyde $C_6H_4(ONa).CHO$ with NaOAc and Ac_2O (Tiemann a. Herzfeld, *B.* 10, 65). Felted groups of slender needles (from hot water). Sublimes readily. Sol. boiling water, alcohol, ether, and HOAc, v. sl. sol. cold water, benzene, and $CHCl_3$.

Carboxy-methyl derivative $C_{11}H_{10}O_5$ *i.e.* $C_6H_4(O.CH_2.CO_2H).CH:CH.CO_2H$ [1:4]. *p-Cumaroxy-acetic acid. Phenyl-glycollic-p-acrylic acid.* [225°]. Prepared by boiling a mixture of *p*-aldehydo-phenoxy-acetic acid (1 pt.), sodium acetate (1 pt.), and acetic anhydride (3 pts.) for 5 hours. Warty crystals. Sol. benzene and benzoline, v. sol. alcohol, ether, and acetic acid, sl. sol. cold water. The Ag, Pb, Cu, and Fe salts are sparingly soluble pps. (Elkan, *B.* 19, 3046).

Di-bromide of coumaric acid *v.* DI-BROMO-OXY-PHENYL-PROPIONIC ACID.

Hydro-coumaric acid *v.* OXY-PHENYL-PROPIONIC ACID.

Other derivatives are described as NITRO-COUMARIC ACID, DI-OXY-CINNAMIC ACID, and OXY-AMIDO-CINNAMIC ACID.

o-**COUMARIC ALDEHYDE**

$C_6H_4(OH).CH:CH.COH$. *Oxy-cinnamic aldehyde.* [133°]. Long slender needles. V. sol. alcohol and ether, sl. sol. water. Fe_2Cl_6 gives a red pp. Formed by the decomposition of its glucoside under the influence of emulsin (Tiemann a. Kees, *B.* 18, 1962).

Glucoside $[2:1]C_6H_4(OC_6H_{11}O_5).C_2H_2.COH$. *Gluco-coumaric aldehyde.* [199°]. Formed by adding a few drops of dilute NaOH to a mixture of helicin $[2:1]C_6H_4(OC_6H_{11}O_5).COH$ and acetic aldehyde. This condensation even takes place in dilute aqueous solution and at a low temperature (Tiemann a. Kees, *B.* 18, 1958). Fine white needles (containing aq). V. sol. hot water and alcohol, insol. ether and chloroform. Lævorotatory. By emulsin it is split up into coumaric aldehyde and glucose. Sodium amalgam reduces it to gluco-coumaryl alcohol

$$C_6H_4(OC_6H_{11}O_5).C_2H_2.CH_2(OH).$$

Phenyl hydrazide of the glucoside $C_6H_4(OC_6H_{11}O_5).C_2H_2.CH:N_2HPh$: [132°]; sol. alcohol and hot water, nearly insol. cold water.

Oxim of the glucoside $C_6H_4(OC_6H_{11}O_5).C_2H_2.CH:NOH$: [230°]; long white needles (containing 2aq); v. sol. hot water, less sol. alcohol, insol. ether.

m-**Coumaric aldehyde** [3:1] $C_6H_4(OH)CH:CH.CHO$. [100°]. From *m*-aldehydo-phenoxy-acetic acid, aldehyde, and dilute NaOHAq (Elkan, *B.* 19, 3048).

p-**Coumaric aldehyde** [4:1] $C_6H_4(OH)CH:CH.CHO$. [182°]. From *p*-aldehydo-phenoxy-acetic acid in the same way.

COUMARILIC ACID $C_9H_6O_3$ *i.e.* $C_6H_4(OH).C{:}C.CO_2H$ or $C_6H_4<\begin{matrix}CH\\O\end{matrix}>C.CO_2H$. *o-Oxy-phenyl-propiolic acid.* [191°] (F.); [193°] (P.). (c. 312°). Formed by treating (α)-bromo-coumarin with hot alcoholic KOH (Perkin, *C. J.* 24, 45; Fittig, *A.* 216, 162). Long needles (from water); v. e. sol. alcohol, m. sol. water, sl. sol. chloroform and CS_2. Not attacked by Br or conc. HBr. Potash-fusion gives salicylic and acetic acids. $KMnO_4$ forms only CO_2. Sodium amalgam reduces it to hydrocoumarilic acid $C_9H_8O_3$.

Salts.—AgA'.—CaA'_2 3aq. BaA'_2 4aq.

Ethyl ether EtA': [27°]; (274° at 720 mm.) (Hantzsch, *B.* 19, 2401).

Methyl derivative $C_6H_4(OMe).C{:}C.CO_2H$. [126°]. From the methyl-derivative of *exo*-bromo-coumaric acid and dilute KOH (Perkin, *C. J.* 39, 423). Needles (from CS_2).

Bromo-coumarilic acid $C_6H_3Br<\begin{matrix}CH\\O\end{matrix}>C.CO_2H$. [250°]. From (α)-di-bromo-coumarin and alcoholic KOH (Perkin, *C. J.* 24, 45). Needles, sl. sol. water, v. sol. alcohol.

Methyl derivative $C_6H_4Br(OMe).C{:}C.CO_2H$. [168°]. Prepared from $C_6H_3Br(OMe).C_2H_2Br_2.CO_2H$ and aqueous KOH (Perkin, *C. J.* 39, 419). Small needles (from benzene).

p-**Oxy-cumarilic acid** *Methyl derivative* $C_6H_3(OMe)<\begin{matrix}CH\\O\end{matrix}>C.CO_2H$ [4:2:1]. [196°]. Formed by boiling bromo-umbelliferon-methyl ether $C_6H_3(OMe)<\begin{matrix}CH:CBr\\ \diagup\\ O.CO\end{matrix}$ with conc. alcoholic KOH. Long white needles. V. sol. alcohol and ether, scarcely sol. cold water, more readily in hot. Slightly volatile with steam.—BaA'_2 4aq: white crystalline solid (Will a. Beck, *B.* 19, 1783).

Ethyl derivative $C_{11}H_{10}O_4$ *i.e.* $C_6H_3(OEt)<\begin{matrix}CH\\O\end{matrix}>C.CO_2H$ [4:2:1]. [163°]. Formed by boiling bromo-umbelliferon-ethyl ether $C_6H_3(OEt)<\begin{matrix}CH:CBr\\ |\\ O.CO\end{matrix}$ with conc. alcoholic KOH. Long felted needles (Will a. Beck, *B.* 19, 1785).

Hydro-coumarilic acid $C_9H_8O_3$ *i.e.* $C_6H_4<\begin{matrix}CH_2\\O\end{matrix}>CH.CO_2H$. [117°]. (299°). Formed by treating coumarilic acid with sodium amalgam, and extracted by ether from the acidified product (Fittig, *A.* 216, 166). Pearly plates (from water); very volatile with steam. V. sol. alcohol and ether, m. sol. water. Partially decomposed on distillation, yielding a phenol. Gives phenol on distillation with lime.

Salts.—AgA'.—CaA'_2 2aq.—BaA'_2 2aq.

Ethyl ether EtA'. [23°]. (273°).

p-**Oxy-hydrocoumarilic acid** *Methyl derivative* $C_{10}H_{10}O_4$ *i.e.* $C_6H_3(OMe)<\begin{matrix}CH_2\\O\end{matrix}>CH.CO_2H$ [4·2:1]. [114°]. Formed by reduction of the methyl derivative of oxy-coumarilic acid $C_6H_3(OMe)<\begin{matrix}CH\\O\end{matrix}>C.CO_2H$ with sodium-amalgam. Hard prisms. V. sol. ordinary solvents. Volatile with steam (Will a. Beck, *B.* 19, 1783).

Ethyl derivative $C_{11}H_{12}O_4$ *i.e.* $C_6H_3(OEt)<\begin{matrix}CH_2\\O\end{matrix}>CH.CO_2H$ [4:2:1]. [119°]. Formed by reduction of ethoxy-coumarilic acid $C_6H_3(OEt)<\begin{matrix}CH\\O\end{matrix}>C.CO_2H$ with sodium amalgam. Hard white needles (Will a. Beck, *B.* 19, 1785).

Di-oxy-coumarilic acid *Di-ethyl derivative* $C_6H_2(OEt)_2<\begin{matrix}O\\CH\end{matrix}>C.CO_2H$. [195°]. From bromo-æsculetic ether $C_6H_2(OEt)_2<\begin{matrix}O\\C_2HBr\end{matrix}>CO$ and alcoholic KOH (Will, *B.* 16, 2119). Slender needles.

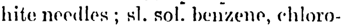
V. also METHYL-COUMARILIC ACID.

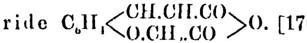
COUMARIN $C_9H_6O_2$ *i.e.* $C_6H_4<\begin{matrix}CH{:}CH\\ \quad |\\ O\,.\,CO\end{matrix}$. Mol. w. 146. [67°]. (290°).

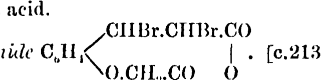
Occurrence.—In Tonka beans, the fruit of *Coumaruma odorata*, or *Dipteryx odorata*, as small white crystals between the seed coating and the kernel; found in woodruff (*Asperula odorata*), in *Melilotus officinalis* (as melilotate $C_{18}H_{16}O_5$ [128°]), in the flowers of sweet-scented vernal grass (*Anthoxanthum odoratum*), in the leaves of Faham (*Angræcum fragrans*), of an-sol. cold water, sl. sol. hot water. V. e. sol. alcohol or ether. The Na salt is oxidised by $KMnO_4$ to ethyl-salicylic aldehyde and ethyl-salicylic acid. Sodium amalgam forms the ethyl derivative of oxy-phenyl propionic acid. Br forms a dibromide [155°]. Salts.—$(C_{11}H_{11}O_3)_2Ca$ 2aq. S. ·43 at 21°.- BaA'_2 4aq. Ethyl ether $C_6H_4(OEt).CH.CH.CO_2Et$. (303°). S.G. $\frac{15}{15}$ 1·09. Formed by treating the preceding with PCl_5, followed by alcohol. Formed also by boiling the (α)-isomeride for some time.

Acetyl derivative $C_6H_4(OAc).CH:CH.CO_2H$. [146°]. Formed by gently heating salicylic aldehyde (3 pts.) with NaOAc (4 pts.) and Ac_2O (5 pts.) (Tiemann a. Herzfeld, *B.* 10, 284). Needles (from water). V. sol. hot water, alcohol, and ether. Converted by dilute KOHAq into coumaric acid; and by heating above 150° into HOAc and coumarin.

Carboxy-methyl derivative $CO_2H.CH_2.O.C_6H_4.CH.CH.CO_2H$. *o-Coumar-oxy-acetic acid.* [190°]. Formed by heating o-aldehydo-phenoxy-acetic acid (1 pt.) with acetic anhydride (5 pts.) and sodium acetate (3 pts.) to boiling for 1 or 2 hours (Rossing, *B.* 17, 2997). Yellow needles. V. sol. alcohol, ether, and hot water, sl. sol. benzene, chloroform, and cold water. Sublimable.

Di-bromide 
$$C_6H_4<\begin{matrix}CHBr.CHBr.CO_2H\\O.CH_2.CO_2H\end{matrix}.$$
[220°]. White needles; sl. sol. benzene, chloroform, and water, v. sol. alcohol and ether.

Anhydride 
$$C_6H_4<\begin{matrix}CH.CH.CO\\O.CH_2.CO\end{matrix}>O.$$
[176°]. Crystalline solid. V. sol. alcohol and ether, sl. sol. water. Formed by heating the acid with phosphoric acid.

Di-bromide 
$$C_6H_4<\begin{matrix}CHBr.CHBr.CO\\ \quad\quad\quad\quad |\\O.CH_2.CO\quad O\end{matrix}.$$
[c.213°]. Orange-yellow needles; v. sol. alcohol and ether, sl. sol. water and benzene (Rossing, *B.* 17, 3001).

Bromo-coumaric acid *v.* vol. i. p. 561.

m-**Coumaric acid** [3:1] $C_6H_4(OH).CH.CH.CO_2H$. [191°]. Formed by heating *m*-oxy-benzaldehyde with acetic anhydride and sodium acetate; or by boiling diazocinnamic acid with water (Tiemann a. Ludwig, *B.* 15, 2018). White prisms. Sol. alcohol, ether, benzene, and hot water.

Acetyl derivative $C_6H_4(OAc).CH.CH.CO_2H$. [151°]. White needles, sol. alcohol, ether, and hot water.

Methyl derivative $C_6H_4(OMe).CH:CH.CO_2H$. [115°]. Long white needles, sol. alcohol, ether, and benzene, sl. sol. hot water (Tiemann a. Ludwig, *B.* 15, 2048).

Carboxy-methyl derivative $C_{11}H_{10}O_5$ *i.e.* $C_6H_4(O.CH_2.CO_2H).CH.CH.CO_2H$ [1:3]. *m-Phenoxy-acetic-acrylic acid. m-Cumaroxy-acetic acid. Phenyl-glycollic-m-acrylic acid.* [219°]. Prepared by heating *m*-aldehydo-phenoxy-acetic acid with sodium acetate and acetic anhydride. White needles (from hot water). V. sol. alcohol, ether, and acetic acid, sl. sol. cold water. The Ag, Pb, Cu, and Fe salts are sparingly soluble pps. (Elkan, *B.* 19, 3047).

p-**Coumaric acid** $C_6H_4(OH).CH:CH.CO_2H$. *p-Oxy-cinnamic acid. p-Oxy-phenyl-acrylic acid. Naringenic acid.* [206°].

Preparation.—1. 2½ kilos. of aloes are boiled for two hours with 5 litres of water and 400 g. conc. H_2SO_4; after cooling the liquor is decanted and the residue again boiled with 2 litres of water, the combined extracts are evaporated to ⅓, and when cold extracted with ether. The crude *p*-coumaric acid (yield: 1·5 to 1·8 p.c.) left on evaporating the ether is purified by conversion into the barium salt (Hlasiwetz, *A.* 136, 31; Eigel, *B.* 20, 2527).—2. *p*-Oxy-benzaldehyde (5 pts.) is heated at 175° with dehydrated sodium acetate (8 pts.) and acetic anhydride (10 pts.); the yield is 70 p.c. of the oxy-benzaldehyde (Tiemann a. Herzfeld, *B.* 10, 63, 283; Eigel). 3. By heating *p*-diazo-cinnamic acid with water; small yield (Gabriel, *B.* 15, 2301).—4. Together with phloroglucin by boiling naringenin with conc. aqueous NaOH (Will, *B.* 20, 299).

Properties. Thick warts (anhy.) or long needles (with *x*aq). V. sl. sol. cold water, v. sol. hot water, v. e. sol. alcohol and ether, sl. sol. benzene, insol. ligroin. Fe_2Cl_6 colours the alcoholic solution brown. Sodium amalgam gives *p*-oxy-phenyl-propionic acid. Potash-fusion forms *p*-oxy-benzoic acid (Barth, *B.* 12, 1259).

Salts.—NH_4A'aq: monoclinic tables.—$CdA'_2$3aq.—$CuA'_2$6aq.—AgA'.

Methyl derivative $C_6H_4(OMe).CH:CH.CO_2H$. [169°] (E.); [171°] (P.). Formed by heating anisic aldehyde with acetic anhydride and sodium acetate at 180° (yield: 70 p.c. of the anisic aldehyde), or by saponification with KOH of the di-methyl-ether $C_6H_4(OMe).CH:CH.CO_2Me$ formed by heating the acid with methyl iodide and KOH. Occurs among the products of the action of KOH and MeI upon tyrosine (Korner a. Menozzi, *G.* 11, 549). Formed also by oxidising the methyl derivative of methyl oxy-styryl ketone with NaOCl (Einhorn a. Grabfield, *A.* 243, 363). Yellow needles, m. sol. alcohol, hot water, and HOAc; sl. sol. cold water and chloroform (Perkin). Gives when heated the methyl derivative of vinyl-phenol $CH_2:CH.C_6H_4OMe$. This body is also formed by successive treatment with HI and Na_2CO_3 (Perkin, *C. J.* 33, 214).—A'Na.—AgA' (Eigel, *B.* 20, 2527).

Methyl ether $C_6H_4(OMe).CH:CH.CO_2Me$. [89°]. (303°). Laminæ. In chloroform solution it takes up bromine, with production of $C_6H_4(OMe)CHBr.CHBr.CO_2Me$ [118°] (Valentini, *G.* 16, 421; Perkin, *C. J.* 39, 439).

Chloride $C_6H_4(OMe).CH:CH.COCl$. [50°].

Amide $C_6H_4(OMe).CH:CH.CONH_2$. [186°].

Acetyl derivative $C_6H_4(OAc).CH:CH.CO_2H$. [c. 195°]. Formed by heating sodium *p*-oxy-benzoic aldehyde $C_6H_4(ONa).CHO$ with NaOAc and Ac_2O (Tiemann a. Herzfeld, *B.* 10, 65). Felted groups of slender needles (from hot water). Sublimes readily. Sol. boiling water, alcohol, ether, and HOAc, v. sl. sol. cold water, benzene, and $CHCl_3$.

Carboxy-methyl derivative $C_{11}H_{10}O_5$ *i.e.* $C_6H_4(O.CH_2.CO_2H).CH:CH.CO_2H$ [1:4]. *p-Cumaroxy-acetic acid. Phenyl-glycollic-p-acrylic acid.* [225°]. Prepared by boiling a mixture of *p*-aldehydo-phenoxy-acetic acid (1 pt.), sodium acetate (1 pt.), and acetic anhydride (3 pts.) for 5 hours. Warty crystals. Sol. benzene and benzoline, v. sol. alcohol, ether, and acetic acid, sl. sol. cold water. The Ag, Pb, Cu, and Fe salts are sparingly soluble pps. (Elkan, *B.* 19, 3046).

Di-bromide of coumaric acid *v.* Di-bromo-oxy-phenyl-propionic acid.

Hydro-coumaric acid *v.* Oxy-phenyl-propionic acid.

Other derivatives are described as Nitro-coumaric acid, Di-oxy-cinnamic acid, and Oxy-amido-cinnamic acid.

o-COUMARIC ALDEHYDE

$C_6H_4(OH).CH:CH.COH$. *Oxy-cinnamic aldehyde.* [133°]. Long slender needles. V. sol. alcohol and ether, sl. sol. water. Fe_2Cl_6 gives a red pp. Formed by the decomposition of its glucoside under the influence of emulsin (Tiemann a. Kees, *B.* 18, 1962).

Glucoside $[2:1]C_6H_4(OC_6H_{11}O_5).C_2H_2.COH$. *Gluco-coumaric aldehyde.* [199°]. Formed by adding a few drops of dilute NaOH to a mixture of helicin $[2:1]C_6H_4(OC_6H_{11}O_5).COH$ and acetic aldehyde. This condensation even takes place in dilute aqueous solution and at a low temperature (Tiemann a. Kees, *B.* 18, 1958). Fine white needles (containing aq). V. sol. hot water and alcohol, insol. ether and chloroform. Lævorotatory. By emulsin it is split up into coumaric aldehyde and glucose. Sodium amalgam reduces it to gluco-coumaryl alcohol

$$C_6H_4(OC_6H_{11}O_5).C_2H_2.CH_2(OH).$$

Phenyl hydrazide of the glucoside $C_6H_4(OC_6H_{11}O_5).C_2H_2.CH:N_2HPh$: [132°]; sol. alcohol and hot water, nearly insol. cold water.

Oxim of the glucoside $C_6H_4(OC_6H_{11}O_5).C_2H_2.CH:NOH$: [230°]; long white needles (containing 2aq); v. sol. hot water, less sol. alcohol, insol. ether.

m-**Coumaric aldehyde**

[3:1] $C_6H_4(OH)CH:CH.CHO$. [100°]. From *m*-aldehydo-phenoxy-acetic acid, aldehyde, and dilute NaOHAq (Elkan, *B.* 19, 3048).

p-**Coumaric aldehyde**

[4:1] $C_6H_4(OH)CH:CH.CHO$. [182°]. From *p*-aldehydo-phenoxy-acetic acid in the same way.

COUMARILIC ACID $C_9H_6O_3$ *i.e.* $C_6H_4(OH).C{:}C.CO_2H$ or $C_6H_4{<}\genfrac{}{}{0pt}{}{CH}{O}{>}C.CO_2H$. *o-Oxy-phenyl-propiolic acid.* [191°] (F.); [193°] (P.). (c. 312°). Formed by treating (α)-bromo-coumarin with hot alcoholic KOH (Perkin, *C. J.* 24, 45; Fittig, *A.* 216, 162). Long needles (from water); v. e. sol. alcohol, m. sol. water, sl. sol. chloroform and CS_2. Not attacked by Br or conc. HBr. Potash-fusion gives salicylic and acetic acids. $KMnO_4$ forms only CO_2. Sodium amalgam reduces it to hydrocoumarilic acid $C_9H_8O_3$.

Salts.—AgA′. CaA′$_2$ 3aq. BaA′$_2$ 4aq.

Ethyl ether EtA′: [27°]; (274° at 720mm.) (Hantzsch, *B.* 19, 2401).

Methyl derivative $C_6H_4(OMe).C{:}C.CO_2H$. [126°]. From the methyl-derivative of *exo*-bromo-coumaric acid and dilute KOH (Perkin, *C. J.* 39, 423). Needles (from CS_2).

Bromo-coumarilic acid

$C_6H_3Br{<}\genfrac{}{}{0pt}{}{CH}{O}{>}C.CO_2H$. [250°]. From (α)-di-bromo-coumarin and alcoholic KOH (Perkin, *C. J.* 24, 45). Needles, sl. sol. water, v. sol. alcohol.

Methyl derivative

$C_6H_3Br(OMe).C{:}C.CO_2H$. [168°]. Prepared from $C_6H_3Br(OMe).C_2H_2Br_2.CO_2H$ and aqueous KOH (Perkin, *C. J.* 39, 419). Small needles (from benzene).

p-**Oxy-cumarilic acid** *Methyl derivative* $C_6H_3(OMe){<}\genfrac{}{}{0pt}{}{CH}{O}{>}C.CO_2H$ [4:2:1]. [196°]. Formed by boiling bromo-umbelliferon-methyl ether $C_6H_3(OMe){<}\begin{array}{c}CH:CBr\\ /\\ O.CO\end{array}$ with conc. alcoholic KOH. Long white needles. V. sol. alcohol and ether, scarcely sol. cold water, more readily in hot. Slightly volatile with steam.—BaA′$_2$ 4aq: white crystalline solid (Will a. Beck, *B.* 19, 1783).

Ethyl derivative $C_{11}H_{10}O_4$ *i.e.* $C_6H_3(OEt){<}\genfrac{}{}{0pt}{}{CH}{O}{>}C.CO_2H$ [4:2:1]. [163°]. Formed by boiling bromo-umbelliferon-ethyl ether $C_6H_3(OEt){<}\begin{array}{c}CH:CBr\\ |\\ O.CO\end{array}$ with conc. alcoholic KOH. Long felted needles (Will a. Beck, *B.* 19, 1785).

Hydro-coumarilic acid $C_9H_8O_3$ *i.e.* $C_6H_4{<}\genfrac{}{}{0pt}{}{CH_2}{O}{>}CH.CO_2H$. [117°]. (299°). Formed by treating coumarilic acid with sodium amalgam, and extracted by ether from the acidified product (Fittig, *A.* 216, 166). Pearly plates (from water); very volatile with steam. V. sol. alcohol and ether, m. sol. water. Partially decomposed on distillation, yielding a phenol. Gives phenol on distillation with lime.

Salts.—AgA′.—CaA′$_2$ 2aq.—BaA′$_2$ 2aq.

Ethyl ether EtA′. [23°]. (273°).

p-**Oxy-hydrocoumarilic acid** *Methyl derivative* $C_{10}H_{10}O_4$ *i.e.* $C_6H_3(OMe){<}\genfrac{}{}{0pt}{}{CH_2}{O}{>}CH.CO_2H$ [4:2:1]. [114°]. Formed by reduction of the methyl derivative of oxy-coumarilic acid $C_6H_3(OMe){<}\genfrac{}{}{0pt}{}{CH}{O}{>}C.CO_2H$ with sodium-amalgam. Hard prisms. V. sol. ordinary solvents. Volatile with steam (Will a. Beck, *B.* 19, 1783).

Ethyl derivative $C_{11}H_{12}O_4$ *i.e.* $C_6H_3(OEt){<}\genfrac{}{}{0pt}{}{CH_2}{O}{>}CH.CO_2H$ [4:2:1]. [119°]. Formed by reduction of ethoxy-coumarilic acid $C_6H_3(OEt){<}\genfrac{}{}{0pt}{}{CH}{O}{>}C.CO_2H$ with sodium amalgam. Hard white needles (Will a. Beck, *B.* 19, 1785).

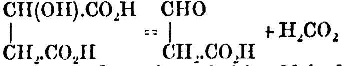
Di-oxy-coumarilic acid *Di-ethyl derivative* $C_6H_2(OEt)_2{<}\genfrac{}{}{0pt}{}{O}{CH}{>}C.CO_2H$. [195°]. From bromo-æsculetic ether $C_6H_2(OEt)_2{<}\genfrac{}{}{0pt}{}{O\text{———}}{C_2HBr}{>}CO$ and alcoholic KOH (Will, *B.* 16, 2119). Slender needles.

V. also Methyl-coumarilic acid.

COUMARIN $C_9H_6O_2$ *i.e.* $C_6H_4{<}\begin{array}{c}CH:CH\\ |\\ O\ .\ CO\end{array}$. Mol. w. 146. [67°]. (290°).

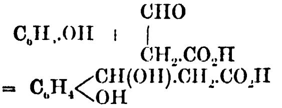
Occurrence.—In Tonka beans, the fruit of *Coumaruma odorata*, or *Dipteryx odorata*, as small white crystals between the seed coating and the kernel; found in woodruff (*Asperula odorata*), in *Melilotus officinalis* (as melilotate $C_{18}H_{16}O_5$ [128°]), in the flowers of sweet-scented vernal grass (*Anthoxanthum odoratum*), in the leaves of Faham (*Angræcum fragrans*), of an other orchid, *Orchis fusca*, and of *Liatris odoratissima* (Guibourt, *Histoire des Drogues Simples*; Boullay a. Boutron-Chaillard, *J. Ph.* 9, 480; Delalande, *A. Ch.* [3] 6, 343; Bleibtreu, *A.* 59, 177; Procter, *Rép. chim. App.* 1861, 143; Fontana, *B. J.* 14, 311; Guillemette, *A.* 14, 328; Kossmann, *A.* 52, 387; Gobley, *A.* 76, 354).

Formation.—1. By boiling salicylic aldehyde with Ac_2O and NaOAc (Perkin, *C. J.* 21, 53, 181; *cf.* vol. i. p. 158).—2. Together with HOAc by heating acetyl-coumaric acid (Tiemann a. Herzfeld, *B.* 10, 287). -3. By the action of Br at 170° on the anhydride of *o*-oxy-phenyl-propionic acid (Hochstetter, *A.* 226, 360).—4. By heating phenol with malic acid and H_2SO_4 or $ZnCl_2$. The reaction probably takes place in the following stages: (1) By splitting off formic acid the semi-aldehyde of malonic acid is formed.



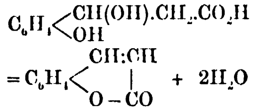
$$\begin{matrix}CH(OH).CO_2H\\ |\\ CH_2.CO_2H\end{matrix} = \begin{matrix}CHO\\ |\\ CH_2.CO_2H\end{matrix} + H_2CO_2$$

(2) By condensation of this aldehyde with the phenol an oxy-phenyl-lactic acid is produced -



$$C_6H_5.OH + \begin{matrix}CHO\\ |\\ CH_2.CO_2H\end{matrix} = C_6H_4\langle\begin{matrix}CH(OH).CH_2.CO_2H\\ OH\end{matrix}$$

(3) By splitting two mols. of water from this body a cumarin is formed:



$$C_6H_4\langle\begin{matrix}CH(OH).CH_2.CO_2H\\ OH\end{matrix} = C_6H_4\langle\begin{matrix}CH{:}CH\\ \quad |\\ O-CO\end{matrix} + 2H_2O$$

(Pechmann, *B.* 17, 929).

Properties. - - Triclinic crystals, *a*:*b*:*c* = ·8833:1:·3696 (Scacchi, *G.* 14, 568). Peculiar odour. M. sol. hot water, v. e. sol. alcohol, insol. cold aqueous baryta, but dissolves on boiling. Ether will not extract it from the solution, but acids, even CO_2, re-ppt. it. It appears, however, to have formed the barium salt of an oxy- acid, which is not *o*-coumaric acid, unless the boiling is prolonged after the coumarin is dissolved (Ebert, *A.* 216, 139). Coumarin dissolves in boiling aqueous K_2CO_3 without evolution of CO_2, apparently forming a compound with it. $BaCO_3$ has no action on coumarin.

Reactions.—1. Boiling conc. aqueous KOH gives *o*-coumaric acid. 2. *Potash-fusion* forms acetic and salicylic acids.—3. Gaseous HBr passed into its solution forms large transparent crystals [c. 15°] of what is probably an addition-product. Exposed to the air, these crystals quickly lose HBr, leaving pure coumarin (Ebert, *A.* 226, 347).—4. *Sodium amalgam* reduces it to oxy-phenyl-propionic acid. In alcoholic solution sodium amalgam forms di-hydro-di-coumaric acid $C_{18}H_{18}O_6$, which is sl. sol. cold water, forms the salts Na_2A'' 10aq, CaA'' 2aq, PbA'', CuA'' 2aq, and Ag_2A'', and an anhydride $C_{18}H_{16}O_5$ [222°] (Zwenger, *A. Suppl.* 8, 32).

Combinations with bases. $C_9H_6O_2 2KOH$.—$C_9H_6O_2 2NaOH$. Obtained by boiling coumarin (1 mol.) with aqueous NaOH (2 mols.) for a few minutes. Deliquescent; at 150° it becomes $C_9H_6O_2Na_2O$.—$C_9H_6O_2Ba(OH)_2$.—$C_9H_6O_2 2PbO$.—$C_9H_6O_2Ag_2O$: yellow pp. Formed by adding $AgNO_3$ to the yellow solution of coumarin in aqueous KOH (Perkin, *C. J.* 22, 192; Williamson, *C. J.* 28, 850).

Oxim $C_6H_4\langle\begin{smallmatrix}C_2H_2\\ O\end{smallmatrix}\rangle C(NOH)$: [131°]. Formed by the action of hydroxylamine upon thiocoumarin in alcoholic solution. Long white needles. V. sol. alcohol, ether, and benzene; sol. hot water, nearly insol. cold. It is very stable to alkalis and acids, but by long heating with HCl it is split up into coumarin and H_2NOH.

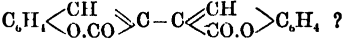
Ethyl-oxim $C_6H_4\langle\begin{smallmatrix}C_2H_2\\ O\end{smallmatrix}\rangle C(NOEt)$: [50°]. Formed by ethylation of the oxim. Colourless plates. V. sol. alcohol, ether, and benzene, insol. water.

Phenyl-hydrazide $C_6H_4\langle\begin{smallmatrix}C_2H_2\\ O\end{smallmatrix}\rangle C(N_2HPh)$: [144°]. Formed by heating thiocoumarin with phenyl-hydrazine in alcoholic solution. Long yellow needles. V. sol. benzene and ether, sol. hot alcohol, sl. sol. cold alcohol, insol. water. Dissolves in H_2SO_4 with a green colour (Tiemann, *B.* 19, 1662).

Coumarin bromide $C_9H_6O_2Br_2$. [105°]. From coumarin (7 pts.) and Br (8 pts.) in CS_2 (Perkin, *C. J.* 17, 368; 9, 37). Oblique prisms (from alcohol); v. sol. alcohol, but decomposed by boiling therewith. Gives off Br a little above its melting-point. Alcoholic KOH converts it into (*α*)-bromo-coumarin (*v.* vol. i. p. 564).

Chloro-coumarin *v.* p. 57.

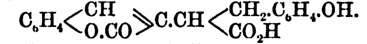
Di-coumarin $C_{18}H_{10}O_4$ *i.e.*



$$C_6H_4\langle\begin{matrix}CH\\ O.CO\end{matrix}\rangle\!\!\!\rangle C-C\langle\!\!\!\langle\begin{matrix}CH\\ CO.O\end{matrix}\rangle C_6H_4 \ ?$$

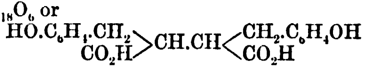
[above 330°]. From salicylic aldehyde, sodium succinate, and Ac_2O at 100° (Dyson, *C. J.* 51, 62). Insol. ether, alcohol, and benzene, sl. sol. chloroform, and HOAc. Slowly dissolves in boiling NaOHAq, but is reppd. unchanged by acids. Reduced in alkaline solution by sodium amalgam to hydro-di-coumaric acid $C_{18}H_{14}O_5$, which is insol. water, sol. $CHCl_3$ and benzene. It forms the salts $BaA'_2$6aq and AgA'. At 133° hydrodicoumaric acid splits up into water and its anhydride hydrodicoumarin $C_{18}H_{12}O_4$ [256°]. It is reconverted into the acid by long heating with conc. NaOHAq or with HOAc. Bromine acting on hydrodicoumarin in $CHCl_3$ forms $C_{18}H_{11}BrO_4$.

Hydro-dicoumaric acid is perhaps



$$C_6H_4\langle\begin{matrix}CH\\ O.CO\end{matrix}\rangle\!\!\!\rangle C.CH\langle\begin{matrix}CH_2.C_6H_4.OH.\\ CO_2H\end{matrix}$$

Reduced in aqueous alkaline solution by sodium amalgam it gives the dihydro-dicoumaric acid $C_{18}H_{18}O_6$ or



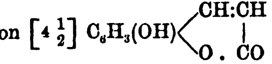
$$\begin{matrix}HO.C_6H_4.CH_2\\ CO_2H\end{matrix}\rangle CH.CH\langle\begin{matrix}CH_2.C_6H_4OH\\ CO_2H\end{matrix}$$

not identical with Zwenger's acid. Its salts are $CaA'_2$6aq.—Ag_2A''. It forms an anhydride $C_{18}H_{14}O_4$ [224°].

Homologues of coumarin. Obtained by the action of fatty anhydrides upon sodium *o*-oxybenzoic aldehyde (Perkin, *C. J.* 28, 10). They are described as anhydrides of the corresponding oxy- acids.

Oxy-coumarins. Described as *anhydrides* of DI-OXY-CINNAMIC ACID, &c. The di-oxy-benzenes and their homologues may be converted by treatment with malic acid and H_2SO_4 into oxy-coumarins, and by aceto-acetic ether and a dehydrating agent into oxy-methyl-coumarins. When excess of aceto-acetic ether is used, small quantities of polycoumarins are also formed (Pechmann, *B.* 17, 929, 2191; 20, 1328).

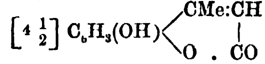
Thus from resorcin may be prepared umbelliferon



$$\left[4\ \tfrac{1}{2}\right]\ C_6H_3(OH)<\begin{array}{l}CH{:}CH\\ \qquad\ |\\ O\ .\ CO\end{array}$$

[224°],

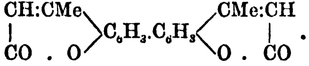
(*β*)-methyl-umbelliferon



$$\left[4\ \tfrac{1}{2}\right]\ C_6H_3(OH)<\begin{array}{l}CMe{:}CH\\ \qquad\ |\\ O\ .\ CO\end{array}$$

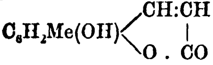
[218°],

and di-methyl-di-coumarin



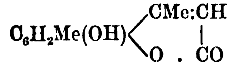
$$\begin{array}{l}CH{:}CMe\\ |\\ CO\ .\ O\end{array}>C_6H_3.C_6H_3<\begin{array}{l}CMe{:}CH\\ \qquad\ |\\ O\ .\ CO\end{array}.$$

Orcin gives rise to



$$C_6H_2Me(OH)<\begin{array}{l}CH{:}CH\\ \qquad\ |\\ O\ .\ CO\end{array}$$

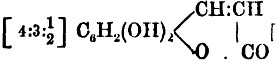
[218°] and



$$C_6H_2Me(OH)<\begin{array}{l}CMe{:}CH\\ \qquad\ |\\ O\ .\ CO\end{array}$$

[250°].

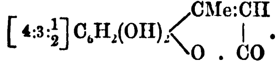
Pyrogallol forms daphnetin



$$\left[4{:}3{:}\tfrac{1}{2}\right]\ C_6H_2(OH)_2<\begin{array}{l}CH{:}CH\\ \qquad\ |\\ O\ .\ CO\end{array}$$

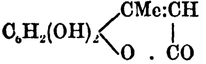
[255°], and

(*β*)-methyl-daphnetin



$$\left[4{:}3{:}\tfrac{1}{2}\right]C_6H_2(OH)_2<\begin{array}{l}CMe{:}CH\\ \qquad\ |\\ O\ .\ CO\end{array}.$$

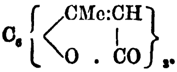
Phloroglucin gives



$$C_6H_2(OH)_2<\begin{array}{l}CMe{:}CH\\ \qquad\ |\\ O\ .\ CO\end{array}$$

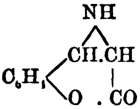
[284°], and

'tri-methyl-tri-coumarin'



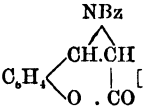
$$C_6\left\{<\begin{array}{l}CMe{:}CH\\ \qquad\ |\\ O\ .\ CO\end{array}\right\}_3.$$

Imido-dihydro-coumarin



$$C_6H_4<\begin{array}{l}\quad\overset{NH}{\wedge}\\ CH.CH\\ \qquad |\\ O\ .\ CO\end{array}$$

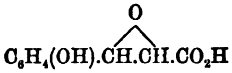
Benzoyl derivative



$$C_6H_4<\begin{array}{l}\quad\overset{NBz}{\wedge}\\ CH.CH\\ \qquad |\\ O\ .\ CO\end{array}$$

[171°].

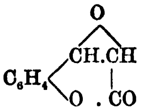
Fine white needles; sol. warm ether, alcohol, benzene and acetic acid; insol. water. Formed by boiling an acetic acid solution of the benzoyl derivative of *o*-oxy-phenyl-*αβ*-imido-propionic anhydride $\left\{C_6H_4(OH).C_2H_2(NBz).CO\right\}_2O$. By treatment with concentrated aqueous NaOH it is converted into *o*-oxy-phenyl-glycidic acid



$$C_6H_4(OH).\overset{\overset{O}{\wedge}}{CH.CH}.CO_2H$$

(Plöchl a. Wolfrum, *B.* 18, 1184; *cf.* Rebuffat, *G.* 15, 527).

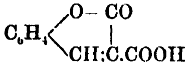
Cumarin oxide



$$C_6H_4<\begin{array}{l}\quad\overset{O}{\wedge}\\ CH.CH\\ \qquad |\\ O\ .\ CO\end{array}$$

Inner anhydride of o-oxy-phenyl-glycidic acid. [153°]. Long needles or prisms. V. sol. ether and warm alcohol. Formed by boiling *o*-oxy-phenyl-glycidic acid with dilute H_2SO_4. By boiling with water it is partly converted back again into oxy-phenyl-glycidic acid (Plöchl a. Wolfrum, *B.* 18, 1187).

COUMARIN - CARBOXYLIC ACID



$$C_6H_4<\begin{array}{l}O-CO\\ \quad\ |\\ CH{:}C.COOH\end{array}$$

[187°].

Formed by heating salicylic aldehyde, malonic acid, and glacial HOAc at 100° (Stuart, *C. J.* 49, 366). White needles (from water). It is not decomposed by boiling with water or on melting, but on heating above 190° it evolves CO_2, leaving coumarin.

Salts.—BaA'_2 and AgA' are white pps.

COUMARIN DIHYDRIDE *v. Anhydride of* OXY-PHENYL-PROPIONIC ACID.

COUMARONE C_8H_6O *i.e.* $C_6H_4<\begin{smallmatrix}CH\\ O\end{smallmatrix}>CH$. (169°). Formed by heating coumarilic acid with lime, CO_2 being split off (Fittig a. Ebert, *A.* 216, 168; 226, 347). Formed also by boiling *o*-aldehydo-phenoxy-acetic acid with Ac_2O and NaOAc (Rössing, *B.* 17, 3000). Heavy oil; volatile with steam. Not attacked by sodium amalgam. Converted by a drop of H_2SO_4 into a reddish-white amorphous mass.

Dibromide $C_8H_6OBr_2$. [86°]. Prisms (from CS_2). Converted by boiling with water into coumarone and other products.

Bromo-coumarone C_8H_5BrO. [36°]. From coumarone dibromide and alcoholic KOH. Needles (from dilute alcohol). V. e. sol. alcohol and ether, insol. water and alkalis.

p-**Methoxy-coumarone** $C_9H_8O_2$ *i.e.* $C_6H_3(OMe)<\begin{smallmatrix}CH\\ O\end{smallmatrix}>CH$ [4:2:1]. (179°). Formed by dry-distillation of the silver salt of methoxy-coumarilic acid $C_6H_3(OMe)<\begin{smallmatrix}CH\\ O\end{smallmatrix}>C.CO_2H$ in a stream of CO_2. Colourless oil, having a strong odour of flowers. Somewhat heavier than water. Very volatile with steam (Will a. Beck, *B.* 19, 1784).

Oxy-methyl-coumarone $C_9H_8O_2$ *i.e.* $\left[4\ \tfrac{1}{2}\right]\ C_6H_3(OH)<\begin{smallmatrix}CMe\\ O\end{smallmatrix}>CH$. [97°]. Formed, by loss of CO_2, by distillation of oxy-methyl-coumarilic acid $C_6H_3(OH)<\begin{smallmatrix}CMe\\ O\end{smallmatrix}>C.CO_2H$. White needles. Sol. benzene and hot water, v. e. sol. alcohol and ether. Dissolves in alkalis without alteration. Sparingly volatile with steam. Sublimes slowly at the ordinary temperature. Gives a violet colouration on warming with conc. H_2SO_4 (Hantzsch, *B.* 19, 2929).

Coumarone-*α*-carboxylic acids are identical with COUMARILIC ACIDS (*q. v.*).

o-**COUMARYL-ALCOHOL.** *Glucoside.* $C_6H_4(OC_6H_{11}O_5).C_2H_2.CH_2OH$. *Gluco-coumaryl alcohol.* [115°]. Fine white needles (containing aq). V. sol. alcohol, insol. ether. Formed by reduction of gluco-*o*-coumaric aldehyde with sodium amalgam. By emulsin it is split up into coumaryl alcohol (which is an oil) and glucose (Tiemann a. Kees, *B.* 18, 1962).

CREATINE $C_4H_9N_3O_2$ *i.e.* $NH_2.C(NH).NMe.CH_2.CO_2H$. Mol. w. 131. *Methyl-guanido-acetic acid.* S.G. 1·35. S 1·3 at 18°. S. (alcohol) ·016.

Occurrence.—In the muscular flesh of mammalia, birds, amphibia, and fishes (Chevreul, *J. Ph.* 21, 234; Pettenkofer, *A.* 52, 97; Liebig, *A.* 62, 282; 108, 354; Heintz, *P.* 62, 602; 70, 460; 73, 596; 74, 125; *C. R.* 24, 500; Gregory, *C. J.* 1, 25; Dessaignes, *C. R.* 38, 839; 41, 1258; *J. Ph.* [3] 32, 41; *A.* 97, 339; Schlossberger, *A.* 49, 344; 66, 80; Price, *C. J.* 3, 229; Stadeler, *J. pr.* 72, 256). Occurs also in urine, blood, and brains (Verdeil a. Marcet, *J. Ph.* [3] 20, 89; Muller, *A.* 103, 142; Voit, *J.* 1867, 791). In some cases where creatine has been found it may have been formed from pre-existent creatinin by the process of extraction. Creatinin does not, however, appear to exist in flesh (Neubauer, *Fr.* 2, 22; Nawrocki, *Fr.* 4, 330).

Synthesis. By the direct union of cyanamide with methyl-amido-acetic acid (sarcosine) in aqueous or alcoholic solution (Volhard, *Z.* [2] 5, 319; Strecker, *J.* 1868, 686).

Preparation.—Finely-chopped meat (250 g.) is heated with water (250 c.c.) at 60° for 10 minutes, the liquid is squeezed out and heated till the albumen is coagulated. The filtrate is treated with lead sub-acetate as long as ppn. occurs, is filtered, and freed from excess of lead by H_2S. The filtrate from PbS is evaporated to a syrup, from which creatine slowly separates; a further quantity may be ppd. by adding alcohol (2 or 3 vols.) (Neubauer, *Fr.* 2, 22; Mulder a. Monthaan, *Z.* [2] 5, 341).

Properties. - Monoclinic prisms (containing aq). Sl. sol. water, v. sl. sol. alcohol, insol. ether. The aqueous solution is neutral to litmus. Converted into its anhydride creatinin by heating with aqueous HCl, with $ZnCl_2$, with H_2SO_4, or even (although slowly) with water at 100°. Gaseous HCl passed over creatine at 100° also forms creatinin hydrochloride. If 5 or 6 drops of a 20 p.c. solution of $AgNO_3$ are added to 2 c.c. of a cold saturated solution of creatine, and a solution of KOH is added so as just to redissolve the white pp. which is first formed, the liquid presently solidifies to a transparent jelly; reduction of silver takes place on heating (Engel, *C. R.* 78, 1707).

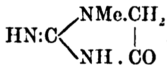
Reactions.—1. Boiling *baryta-water* splits it up into urea (or CO_2 and NH_3) and methyl-amido-acetic acid. Methyl-hydantoin is also formed.—2. *Nitrous acid* decomposes it, giving off half its nitrogen in the free state.—3. Alkaline NaOBr gives off two-thirds of the nitrogen as such (Hufner, *J. pr.* [2] 1, 7).—4. Boiling with water and HgO gives methyl-guanidine and oxalic acid.—5. When heated with soda-lime it gives off methylamine.

Salts.—$B'_2H_2SO_4$: slender prisms.—B'HCl. - $B'HNO_3$: short thick prisms.—$B'CdCl_2$ 2aq: large crystals. $B'ZnCl_2$: small crystals, resolved by hot water into creatine and $ZnCl_2$ (Neubauer, *A.* 137, 298). $HgC_4H_7N_3O_2\ \frac{1}{2}aq$: white pp. from creatine, $HgCl_2$, and KOH (Engel, *C. R.* 80, 885; *B.* 8, 546).

Amphicreatine $C_9H_{19}N_7O_4$. A base occurring in muscular tissue (Gautier, *Bl.* [2] 48, 19). Yellow crystals; not ppd. by $Cu(OAc)_2$ or $HgCl_2$ but ppd. by sodium phosphomolybdate. Its hydrochloride is crystalline but not deliquescent. Its platinochloride forms soluble tables.

Isomeride of creatine *v.* ALACREATINE, vol. i. p. 93.

CREATININE $C_4H_7N_3O$ *i.e.*



$$\mathrm{HN{:}C}\begin{array}{l}\nearrow \mathrm{NMe.CH_2}\\ \qquad\quad |\\ \searrow \mathrm{NH\,.\,CO}\end{array}$$

. Mol. w. 113. S. 9 at 16°. S. (alcohol) 1 at 16° (Liebig); ·3 at 16° (Johnson).

Occurrence.—In human urine to the extent of ·5 p.c. (Pettenkofer, *A.* 52, 97; Heintz, *P.* 62, 602; 73, 595; 74, 125; Liebig, *A.* 62, 298, 324; Neubauer, *A.* 119, 39). Occurs also in urine of horses, calves, and dogs (Heintz; Voit, *C. C.* 1867, 504; Socoloff, *A.* 78, 243; 80, 114; Maly, *A.* 159, 279) and in the flesh of some fish (Krukenberg, *J. Th.* 1881, 344).

Formation.—From creatine by the action of mineral acids or of dehydrating agents.

Preparation.—1. Fresh human urine is neutralised with milk of lime; chloride of calcium added as long as a pp. of phosphate of calcium continues to form; the filtrate evaporated till the salts crystallise out; 32 pts. of the mother-liquor mixed with 1 pt. of chloride of zinc dissolved in the smallest possible quantity of water; the mixture set aside for four days; and the zinc-compound, which separates in nodules, washed with cold water. The zinc-compound is then decomposed by boiling with $Pb(OH)_2$, the filtrate is evaporated, and the mixture of creatine and creatinine digested with cold absolute alcohol, which dissolves the creatinine only (Liebig; Dessaignes, *J. Ph.* [3] 32, 42; Heintz; Loebe, *J. pr.* 82, 170; *Rép. chim. pure*, 1861, 25; Neubauer, *A.* 119, 27; Socoloff, *A.* 78, 243; Grocco, *C. C.* 1887, 17).—2. From urine, after adding $\frac{1}{20}$ vol. saturated aqueous NaOAc, by fractional ppn. with $HgCl_2$. A spherical salt $(C_4H_7HgN_3OHCl)_4 3HgCl_2$ 2aq is obtained, which is suspended in water and decomposed by H_2S. The filtrate on evaporation deposits creatinine hydrochloride, whence $Pb(OH)_2$ liberates creatinine (Johnson, *Pr.* 42, 365; 43, 493).

Properties.—Monoclinic prisms (anhydrous) or efflorescent prisms (containing 2 aq). Neutral to litmus (Salkowski, *H.* 12, 211). V. sol. hot water, m. sol. hot alcohol. According to Johnson (*Pr.* 43, 493) there are two varieties of creatinine, differing in reducing power, solubility, and character of their gold salts. Each exists in efflorescent and in tabular form. 1 part of tabular creatinine from urine dissolves in 10·78 pts. water at 17°, and in 362 pts. alcohol at 17°, and its Pt salt dissolves in 14·1 pts. water at 15°; on the other hand, 1 pt. of tabular creatinine from creatine dissolves in 10·68 pts. water at 16·5°, and in 324 pts. alcohol at 18·5°, while its Pt salt requires 24·4 pts. water at 15°. According to Liebig, 1 pt. creatinine dissolves in 11·5 pts. water at 16°, and in 102 pts. alcohol at 16°.

Reactions.—1. In alkaline solutions it is slowly converted by taking up water into creatine (Dessaignes, *J. Ph.* [3] 32, 41).—2. Boiling with water and HgO gives methyl-guanidine.—3. *Baryta-water* at 100° gives NH_3 and methyl-hydantoin (Neubauer, *A.* 137, 289).—4. $KMnO_4$ gives oxalic acid and methyl-guanidine.

Detection.—1. A small quantity of Fehling's solution at 60° gives a white flocculent pp., consisting of a compound of creatinine with cuprous oxide. 1 mol. creatinine can reduce about $\frac{3}{4}$ mol. CuO (Worm-Muller, *J. Th.* 1881, 76; Maschke, *Fr.* 17, 134). According to Johnson (*Pr.* 42, 365; 43, 493) the creatinine obtained from creatine has not the same reducing power as that from urine, the reducing effect of 2 mols. glucose being equal to that of 5 mols. of the former, but only 4 mols. of the latter. - 2. If a dilute solution of sodium nitroprusside is added to a solution of creatinine and dilute NaOH slowly dropped in, a ruby-red colouration is produced. By this test the presence of creatinine in urine can be demonstrated. With creatine no colour is produced, unless it is previously converted into creatinine by boiling with a dilute acid; in this way the presence of creatine in milk can be proved (Weyl, *B.* 11, 2175). On acidifying and warming prussian blue is formed (Salkowski, *H.* 4, 133; Colasanti, *G.* 17, 129). According to Guareschi (*C. C.* 1887, 580) this reaction is given also by thio-hydantoin, methyl-hydantoin, and other compounds containing the group $N.CH_2.CO.N$.

Salts. $B'HCl$: prisms (from alcohol) or laminæ (from water).—$B'HAuCl_4$. According to Johnson this salt when prepared from creatinine derived from creatine is decomposed by ether, but when prepared from urinary creatinine it is not affected by ether.—$B'_2H_2PtCl_6$ 2aq: orange prisms. Solubility: *v. supra.* $B'HI$: large crystals (from water).—$B'_2H_2SO_4$: dimetric tables (from dilute alcohol).- B'_2ZnCl_2: monoclinic prisms (Schmidt, *A.* 61, 332). Insol. absolute alcohol. S. 1·86 at 15°; 3·65 at 100°. S. (98 p.c. alcohol) ·0108 at c. 18°; S. (87 p.c. alcohol) ·0171 (Neubauer). $B'_2H_2ZnCl_4$: large crystals, v. sol. water and alcohol (Dessaignes, *J. Ph* [3] 32, 43). NaOAc added to its solution pps. B'_2ZnCl_2 (Neubauer, *A.* 120, 267). —B'_2CdCl_2: more soluble in water than B'_2ZnCl_2. - $B'_2Hg(NO_3)_2HgO$: crystalline pp. formed by adding aqueous mercuric nitrate to a conc. solution of creatinine.—$(B'AgNO_3)_2Ag_2O$: delicate white needles (from water).

(*α*)-**Nitroso-creatinine** (?) $C_4H_8N_4O_2$. [210°]. Formed, together with its isomeride, by passing nitrous acid gas into a conc. solution of creatinine. It is much less soluble in water than its (*β*)-isomeride (Dessaignes, *C. R.* 41, 1258; *A.* 97, 339; Marcker, *A.* 133, 305). Crystalline powder, sl. sol. cold water, v. sl. sol. alcohol. HCl at 100° converts it into methyl-parabanic acid, NH_3, and oxalic acid (Strecker, *A.* 118, 151). Br forms $C_4H_7BrN_4O_2$ (?), a neutral crystalline substance, v. sol. water. EtI at 160° followed by Ag_2O gives extremely soluble needles of $C_4H_9NO_4$ [152°]. Salts. -- $B'HCl$ aq. — $B'_2H_2PtCl_6$. — $B'HNO_3$.

(*β*)-**Nitroso-creatinine** $C_4H_8N_4O_2$. [195°]. Formed as above. Nodules, v. sol. water. Salts.—$B'HCl$: laminæ, v. e. sol. cold water.—$B'_2H_2PtCl_6$.

Ethyl-creatinine $C_4H_6EtN_3O$. From creatinine and EtI at 100°, the resulting hydroiodide being decomposed by moist Ag_2O (Neubauer, *A.* 119, 50; 120, 257). Needles (containing $\frac{1}{2}$aq). V. e. sol. alcohol, insol. ether.—$B'HCl$: needles, v. e. sol. alcohol and water, insol. ether.—$B'_2H_2PtCl_6$.—$B'HI$: needles.

Xantho-creatinine $C_8H_{10}N_4O$.

Occurrence.—In muscular tissue (Gautier, *Bl.* [2] 48, 18) and in human urine, especially during fatigue (Monari, *G.* 16, 538).

Properties.—Sulphur-coloured crystals, having a slightly bitter taste. On warming it smells like acetamide. It has a double action on litmus, turning blue litmus red, and sensibly blueing red litmus.

Reactions.—$ZnCl_2$ gives a similar pp. to creatine, B'_2ZnCl_2. $AgNO_3$, a flocculent pp., sol. hot water, crystallising in needles. Ppd. after some time by sodium phosphomolybdate. Its hydrochloride forms feathery crystals; its platinochloride crystallises in long soluble bundles.

Chrusocreatinine *v.* p. 171.

CRENIC ACID (*κρήνη*). Said by Berzelius (*P.* 13, 84; 29, 3, 238) to occur in vegetable mould and in the ochreous deposits of ferruginous waters. The deposit is boiled with potash, and the filtrate treated with HOAc and cupric acetate as long as a dark-brown pp. continues to form. This pp. contains apocrenic acid. The filtrate is neutralised with ammonium carbonate, more cupric acetate is added, and the liquid heated to 80°; cupric crenate is then ppd. Crenic acid is pale yellow and uncrystallisable; apocrenic acid is brown and sl. sol. water. According to Mulder (*A.* 36, 243) crenic acid is $C_{12}H_{12}O_8$, while apocrenic acid is $C_{24}H_{12}O_{12}$. Crenic acid dissolves ferrous carbonate (Boutigny, *C. R.* 58, 247).

CREOSOL $C_8H_{10}O_2$ *i.e.* $C_6H_3Me(OMe)(OH)$ [1:3:4]. Mol. w. 138. (220°). S.G. ^{13} 1·0894. Occurs among the products of the distillation of beech wood and of gum guaiacum (Hlasiwetz, *A.* 106, 339). Formed also by distilling homovanillic acid $C_6H_3(OMe)(OH).CH_2.CO_2H$ with lime (Tiemann a. Nagai, *B.* 10, 206). Aromatic liquid, sl. sol. water, miscible with alcohol, ether, and benzene. Fe_2Cl_6 gives a green colour. HI or potash-fusion convert it into $C_6H_3Me(OH)_2$ (Tiemann a. Koppe, *B* 14, 2025). PCl_5 gives $C_6H_3Me(OMe)Cl$ (?) (185°) S.G. 1·028 which gives a green colour with Fe_2Cl_6 and a pp. of AgCl with $AgNO_3$ (Biechele, *A.* 151, 115).

Salts. $KC_8H_9O_2$ 2aq: needles, v. sol. water and alcohol. -KHA'_2aq: thin prisms; decomposed by water into KA′ and creosol. BaA'_2 3aq: small scales.

Methyl ether $C_6H_3Me(OMe)_2$. (218°). Occurs in beech wood creosote (Tiemann a. Mendelsohn, *B.* 8, 1137). Formed by fusing papaverine with KOH (Goldschmiedt, *M.* 4, 705). Also from creosol, KOH, and MeI. Gives no colour with Fe_2Cl_6.

Ethyl ether $C_6H_3Me(OMe)(OEt)$. Oil.

Acetyl derivative $C_6H_3Me(OMe)(OAc)$. (247°). Oil (Tiemann, *B.* 9, 418; 10, 58).

CREOSOL SULPHONIC ACID $C_6H_2Me(OMe)(OH)(SO_3H)$. From creosol and conc. H_2SO_4 at 60° (Biechele, *A.* 151, 109; Tiemann a. Koppe, *B.* 14, 2026). Hygroscopic syrup.—KA′: needles; its aqueous solution is coloured blue by Fe_2Cl_6.—BaA'_2.- PbA'_2.

CREOSOL CARBOXYLIC ACID *v. Methyl derivative* of DI-OXY-TOLUIC ACID.

CREOSOTE (*κρέας σώζειν*).- A mixture of substances of a phenolic character, which may be extracted by alkalis from the tar obtained by the dry distillation of wood. Rhenish beech tar creosote contains phenol, cresols, guaiacol, phlorol, and creosol (Reichenbach, *Schw. J.* 66, 301, 345; 67, 1, 57; 68, 352; Ettling, *A.* 6, 209; Laurent, *C.R.* 11, 124; 19, 574; Deville, *A. Ch.* [3] 12, 228; Gorup-Besanez, *A.* 78, 231; 86, 223; 143, 129; *Z.* [2] 4, 393; Voelckel, *A.* 86, 93; 87, 306; Hlasiwetz, *A.* 106, 339; Simon, *P.* 32, 129; Hubschmann, *A.* 11, 40; Kone, *A.* 16, 63; Flückiger, *Ph.* [3] 2, 1008; Ruot, *Bl.* [2] 8, 375; H. Muller, *Z.* 1864, 40; Marasse, *B.* 1, 99; 2, 71; *Z.* [2] 4, 502; 5, 348; Frisch, *J. pr.* 100, 223; J. Williams, *C. C.* 1873, 167; Hofmann, *B.* 8, 66; Tiemann a. Mendelsohn, *B.* 8, 1136; Clark, *Ph.* [3] 3, 1037; Watzel, *Ar. Ph.* [3] 10, 130).

CRESAURIN *v. Anhydride of* TRI-OXY-TRI-TOLYL-CARBINOL.

CRESOLS C_7H_8O *i.e.* $C_6H_4Me(OH)$. Mol. w. 108. *Oxy-toluenes. Methyl phenols.* The three cresols occur in the tar obtained by the destructive distillation of coal, beech wood, and pine wood (Schotten a. Tiemann, *B.* 11, 783; Schulze, *B.* 20, 410; Duclos, *A.* 109, 136; Marasse, *A.* 152, 64). They are best obtained in a state of purity from the corresponding toluidines by the diazo- reaction, or from the toluene sulphonic acids by potash-fusion. A cresol is formed by oxidising toluene in presence of Al_2Cl_6 (Friedel a. Crafts, *C. R.* 86, 884). Acid sulphates of the three cresols occur in horse's urine, and cresols are converted into such acids when given to animals in their food (Baumann a. Herter, *B.* 9, 1389). The three cresols, by heating with ammoniacal $ZnBr_2$ and NH_4Br, or with ammoniacal $ZnCl_2$ and NH_4Cl, are converted into the corresponding toluidines and di-tolyl-amines in variable proportion (Merz a. Müller, *B.* 20, 544).

Azo-compounds of the three cresols.- *p* Cresol combines with diazo- compounds as easily as phenols not substituted in the *p*-position, the diazo- residue entering the *o*-position to the OH. Disazo- compounds of *p*-cresol cannot be obtained. In the azo- compounds of *o*- and *m*-cresol the diazo- residue takes the *p*- position to the OH. Both readily yield disazo- compounds, in which the two azo- residues stand in the *p*- and *o*- position to the hydroxyl, and hence are *meta* to each other. *o*- and *m*-Cresol readily give nitroso-derivatives, but *p*-cresol does not (Nolting a. Kohn, *B.* 17, 351).

***o*-Cresol** $C_6H_4Me(OH)[2:1]$. [30°]. (190·8°). S.G. $^{65\cdot6}$ 1·0053; $\frac{0}{0}$ 1·0578. C.E. (0°–10°) ·00072 (Pinette, *A.* 243, 37). H. F. 50,992 (liquid); −3250 (solid) (Stohmann, *J. pr.* [2] 34, 311).

Formation. - 1. By fusing toluene *o*-sulphonic acid with KOH (Engelhardt a. Latschinoff, *Z.* 1869, 620).—2. From *o*-toluidine.—3. By distilling (1, 2, *x*)-oxy-toluic acids with lime.—4. By heating carvacrol with P_2O_5, and fusing the resulting *o*-tolyl phosphate with KOH (Kekulé, *B.* 7, 1006). - 5. By treating camphor with $ZnCl_2$ (Reuter, *B* 16, 624).

Properties.—Crystalline. Converted by potash-fusion into salicylic acid. $KClO_3$ and HCl give di- and tri- chlorotoluquinone (Southworth, *A.* 168, 273). Br gives $C_6H_2Br_2Me(OH)$ [57°] (Werner, *Bl.* [2] 46, 278). Excess of Br gives $C_6H_2Br_3(OBr)$.

Salt.—$(C_6H_4MeO)_3Al$. From *o*-cresol, Al, and a little iodine (Gladstone a. Tribe, *C. J.* 49, 26). Black, vitreous mass, forming a dark-green solution in benzene, decomposed by water and by alcohol. On distillation it yields di-*o*-tolyl oxide $(C_6H_4Me)_2O$ (c. 275°), *o*-cresol, and a compound $C_{15}H_{14}O$, crystallising in colourless plates.

Benzoyl derivative C_7H_7OBz. Oil.

Methyl ether $C_6H_4Me(OMe)$. (171·3°). S.G. $\frac{0}{0}$ ·9957. S.V. 146·1. C.E. (0°–10°) ·00084 (Pinette, *A.* 243, 37; *cf.* Korner, *Z.* [2] 4, 327).

Ethyl ether $C_6H_4Me(OEt)$. (184·8°). S.G. $\frac{0}{0}$ ·9679. S.V. 170·9. C.E. (0°–10°) ·0009 (Pinette, *A.* 243, 38). From alcohol, EtBr and potassium cresol by boiling (Staedel, *A.* 217, 41). The yield is 67 p.c. Also from diazo-toluene sulphate and absolute alcohol (Remsen a. Orndorff, *Am.* 9, 394). HNO_3 converts it into $C_6H_2(NO_2)_2Me(OEt)$ [51°] and a little $C_6H_2(NO_2)_2Me(OH)$ [82°].

Ethylene ether $(C_7H_7O)_2C_2H_4$. [79°]. White plates, sl. sol. cold alcohol.

Propyl ether $C_6H_4Me(OPr)$. (204·1°). S.G. $\frac{0}{0}$ ·9517. S.V. 195. C.E. (0°–10°) ·00087 (Pinette).

Butyl ether $C_6H_4Me(OC_4H_9)$. (223°). S.G. $\frac{0}{0}$ ·9437. S.V. 218·4. C.E. (0°–10°) ·00092.

Heptyl ether $C_6H_4Me(OC_7H_{15})$. (277·5°). S.G. $\frac{0}{0}$ ·9213. S.V. 292·95. C.E. (0°–10°) ·00083.

Octyl ether $C_6H_4Me(OC_8H_{17})$. (292·9°). S.G. ·9231. S.V. 317·9. C.E. (0°–10°) ·00084.

Benzyl ether v. vol. i. p. 490.

***m*-Cresol** $C_6H_4Me(OH)$. [4°]. (202·8°). S.G. $\frac{0}{0}$ 1·0198. S.V. 123·2. C.E. (0°–10°) ·00078 (Pinette, *A.* 243, 40). μ_A 1·5316 at 25°. H.F. 53,044 (Stohmann, *J. pr.* [2] 34, 311). Occurs in coal-tar cresol, together with its *m*- and *p*-isomerides (Schulze, *B.* 20, 409; *cf.* Ihle, *J. pr.* [2] 14, 442). From thymol (100 g.) and P_2O_5 (40 g.); propylene being given off; the resulting *m*-tolyl-phosphoric acid being fused with KOH. The yield is 51 p.c. (Staedel, *A.* 217, 46; *cf.* Engelhardt a. Latschinoff, *Z.* 1869, 621; Southworth, *A.* 168, 268; Tiemann a. Schotten, *B.* 11, 769). Formed also by distilling *m*-oxy-uvitic acid with lime (Oppenheim a. Pfaff, *B.* 8, 886), and by distilling aluminium thymol (Gladstone a. Tribe, *C. J.* 41, 12). Formed also by the action of dry oxygen upon toluene in presence of Al_2Cl_6 (Friedel a. Crafts, *A. Ch.* [6] 14, 436).

Properties.—Liquid. Can be solidified by throwing a crystal of phenol into the liquid cooled in a freezing-mixture (Staedel, *B.* 18, 3443). Its aqueous solution is coloured bluish-violet by Fe_2Cl_6. Fusion with KOH gives *m*-oxy-benzoic acid. HCl and $KClO_3$ from di-chloro-toluquinone Br (3 mols.) gives $C_6HBr_3Me(OH)$ [82°]; excess of Br forms $C_6HBr_3Me(OBr)$ which liberates iodine from KI (Werner, *Bl.* [2] 46, 276).

Benzoyl derivative C_7H_7OBz. [38°]. (c. 295°).

Methyl ether $C_6H_4Me.(OMe)$. (177·2°) S.G. $\frac{0}{0}$ ·9891. S.V. 147·45. C.E. (0–10°) ·00092 (Pinette, *A.* 243, 40). H.F.p. 39,748 ($C,O_2 = 94$; $H_2,O = 69$) (Stohmann, *J. pr.* [2] 35, 24).

Ethyl ether $C_6H_4Me(OEt)$. (192°). S.G. $\frac{0}{0}$ ·965. S.V. 172. C.E. (0°–10°) ·0009 (Pinette, *A.* 243, 41). From *m*-diazo-toluene sulphate and alcohol (Remsen a. Orndorff, *Am.* 9, 394).

Propyl ether $C_6H_4Me(OPr)$. (210·6°). S.G. $\frac{0}{0}$ ·9184. S.V. 196·2. C.E. (0°–10°) ·0009.

Butyl ether $C_6H_4Me(OC_4H_9)$. (229·2°). S.G. $\frac{0}{0}$ ·9407. S.V. 220·45. C.E. (0°–10°) ·00092.

Heptyl ether $C_6H_4Me(OC_7H_{15})$. (283·2°). S.G. $\frac{0}{0}$ ·9202. S.V. 296·7. C.E. (0°–10°) ·00084.

Octyl ether $C_6H_4Me(OC_8H_{17})$. (298·9°). S.G. $\frac{0}{0}$ ·9194. S.V. 321·95. C.E. (0°–10°) ·00086 (Pinette, *A.* 243, 43).

Benzyl ether v. vol. i. p. 490.

m-Cresyl ether v. DI-*m*-TOLYL OXIDE.

***p*-Cresol** $C_6H_4Me(OH)$. [36°]. (201·8°). S.G. $\frac{65\cdot6}{}$ ·9962; $\frac{0}{0}$ 1·0522. S.V. 128·45. C.E. (0°–10°)

·00086 (Pinette, *A.* 243, 43). H.F. 51,100 (solid); −2459 (liquid) (Stohmann, *J. pr.* [2] 34, 311).

Occurrence.—In coal-tar (H. Buff, *B.* 4, 378). As *p*-tolyl sulphuric acid in urine of horses, of cows, and sometimes of men (Brieger, *H.* 4, 204).

Formation.—1. By fusing its sulphonate with KOH (Wurtz, *A.* 144, 121; 156, 258). If the mixture of sulphonic acids of crude cresol is treated with excess of baryta, basic barium *p*-cresol-sulphonate is ppd. (Armstrong a. Field, *C. N.* 29, 282; Baumann, *H.* 6, 185).—2. From *p*-toluidine.—3. Got by putrefaction of ox-brain at 40° (F. Stöckly, *J. pr.* [2] 24, 17). Found also among the products of putrefaction of horses' liver, tyrosine, *p*-oxy-phenyl-acetic acid, and *p*-oxy-phenyl-propionic acid (Baumann a. Brieger, *H.* 3, 149; 4, 304; Weyl, *H.* 3, 312).—4. Together with carpene by the dry distillation of podocarpic acid or its Ca salt (Oudemans, *A.* 170, 259).—5. By heating *p*-oxy-phenyl-acetic acid with CaO (Salkowski, *B.* 12, 1440).

Preparation.—From *p*-toluidine by diazotisation in presence of excess of H_2SO_4.

Properties.—Prisms. Its aqueous solution is coloured blue by Fe_2Cl_6. Potash-fusion converts it into *p*-oxy-benzoic acid. HCl and $KClO_3$ give no chlorinated toluquinone (Southworth, *A.* 168, 271). Br (2 mols.) gives a pp. of $C_6H_2Br_2Me(OH)$ [49°], but a larger quantity of Br (3 mols.) gives $C_6H_2Br_2Me(OBr)$, while a large excess forms $C_6H_2Br_3(OH)$ (Werner, *Bl.* [2] 46, 278). Chloral forms $C_7H_8OC_2HCl_3O$ [52°–56°] (Mazzara, *G.* 13, 272).

Salt.—$(C_6H_4MeO)_3Al$. On distillation it gives a small quantity of di-*p*-tolyl oxide and a ketone $C_{15}H_{14}O$ [168°] (307°). S. (alcohol) ·4 at 20°; 2·5 at 78°. S. (benzene) 3·3 at 21°. V.D. 209·1 (Gladstone, *C. J.* 41, 8).

Acetyl derivative C_7H_7OAc. (c. 210°). Oil (Fuchs, *B.* 2, 626).

Benzoyl derivative C_7H_7OBz. [70·6°]. H.F. 69,010 (Stohmann, *J. pr.* [2] 36, 8; *cf.* Guareschi, *A.* 171, 142).

Lauryl derivative $C_7H_7O.C_{12}H_{25}O$. [28°]. (220°) at 15 mm. (Kraft a. Bürger, *B.* 17, 1378).

Myristyl derivative $C_7H_7O.C_{14}H_{27}O$. [39°]. (240°) at 15 mm. (K. a. B.).

Palmityl derivative $C_7H_7O.C_{16}H_{31}O$. [47°]. (258°) at 15 mm.

Stearyl derivative $C_7H_7O.C_{18}H_{35}O$. [54°]. (276°) at 15 mm. (K. a. B.).

Methyl ether $C_6H_4Me(OMe)$. (175°). S.G. $\frac{0}{0}$ ·9868. S.V. 147·7. C.E. (0–10°) ·00084 (Pinette, *A.* 243, 44; Körner, *Bull. Acad. Belg.* [2] 24, 154).

Ethyl ether $C_6H_4Me(OEt)$. (189·9°). S.G. $\frac{0}{0}$ ·9662. S.V. 172·1. C.E. (0°–10°) ·00086 (Pinette, *A.* 243, 44). H.F.p. 46,880 (Stohmann, *J. pr.* [2] 35, 24). Formed (11½ p.c.), together with aldehyde and toluene (18 p.c.), by decomposing *p*-diazo-toluene sulphate with alcohol (Remsen a. Orndorff, *Am.* 9, 394). HNO_3 (S.G. 1·5) converts it into di-nitro-*p*-cresol [84°] and its ether [75°] (Staedel, *B.* 14, 898). $K_2Cr_2O_7$ and HOAc form [4:1] $C_6H_4(OEt)CO_2H$.

Ethylene ether $(C_6H_4MeO)_2C_2H_4$. [135°]. (297°) (Fuchs, *B.* 2, 624).

Propyl ether $C_6H_4Me(OPr)$. (210·4°). S.G. $\frac{0}{0}$ ·9497. S.V. 196. C.E. (0°–10°) ·00089 (Pinette, *A.* 243, 45).

Butyl ether $C_6H_4Me(OC_4H_9)$. (229·5°). S.G. $\frac{0}{0}$ ·9419. S.V. 220·8. C.E. (0°–10°) ·00092.

Heptyl ether $C_6H_4Me(OC_7H_{15})$. (283·3°). S.G. $\frac{0}{0}$ ·9228. S.V. 297·7. C.E. (0°–10°) ·0009.

Octyl ether $C_6H_4Me(OC_8H_{17})$. (298°). S.G. $\frac{0}{0}$ ·9199. S.V. 322·4. C.E. (0°–10°) ·00088.

Benzyl ether v. vol. i. p. 490.

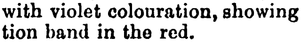
Nitro-benzyl ether v. p-Tolyl nitro benzyl oxide.

p-Cresyl ether v. Di-*p*-tolyl oxide.

Derivatives of cresols *v.* Amido-cresol, Bromo-cresol, Chloro-cresol, Iodo-cresol, Nitro-cresol.

CRESOL DICARBOXYLIC ACIDS *v.* Oxy-uvitic, Oxy-methyl-iso-phthalic, and Oxy-methyl-terephthalic acids.

o-**CRESOL-PHTHALEÏN** $C_{22}H_{18}O_4$ *i.e.*



$(C_6H_3MeOH)_2C{<}\substack{C_6H_4\\ O}{>}CO$. [214°].

Preparation.—By heating *o*-cresol (2 pts.), phthalic anhydride (3 pts.), and stannic chloride (2 pts.) at 120°–125°. From the fused mass thus obtained the undecomposed cresol is separated by steam-distillation; and the phthalein is purified by recrystallisation from alcohol (Baeyer a. Fraude, *A.* 202, 153).

Properties.—Flesh-red crystals, v. sol. alcohol and ether, m. sol. hot water; sol. caustic alkalis with violet colouration, showing a broad absorption band in the red.

Reactions.—1. With *bromine* it forms a di-bromo-derivative together with a bromo-oxy-toluyl-benzoic acid $CO_2H.C_6H_4.CO.C_6H_2MeBr(OH)$ [228°].—2. With *nitric acid* it gives a di-nitro-derivative.—3. *Zinc-dust* forms the corresponding phthalin.—4. *Phthalic anhydride* and *conc. sulphuric acid* give oxy-methyl-anthraquinone.

Di-acetyl derivative $C_{22}H_{16}Ac_2O_4$. [75°]: white amorphous mass.

Di-benzoyl derivative $C_{22}H_{16}Bz_2O_4$. [196°].

Di-bromo-derivative $C_{22}H_{16}Br_2O_4$. [255°]. Crystalline. Sol. alkalis with blue, and in conc. sulphuric acid with rose-red, colouration. Converted by phthalic anhydride and sulphuric acid to bromo-oxy-methyl-anthraquinone.

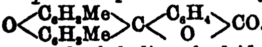
Di-nitro- derivative $C_{22}H_{16}(NO_2)_2O_4$ [248°]: yellow crystals. Sol. Na_2CO_3Aq with red-brown colouration.

o-**Cresol-phthalin** $C_{22}H_{20}O_4$ *i.e.* $(C_6H_3Me.OH)_2CH.C_6H_4.CO_2H$. [218°]. Prepared by reduction of *o*-cresol phthaleïn with zinc-dust and KOH (Fraude, *A.* 202, 168; *B.* 12, 243). Small concentrically grouped needles; sol. water and alcohol, slowly oxidised to *o*-cresol-phthalein by exposure to air. By the action of H_2SO_4 it gives *o*-cresol phthalidin.

Di-acetyl derivative $C_{20}H_{18}Ac_2O_4$. [139°]. Crystalline powder. Sol. acetone. Converted by conc. H_2SO_4 into the phthalidin.

Di-bromo-derivative $C_{20}H_{18}Br_2O_4$. [236°].

p-**Cresol-phthaleïn anhydride** $C_{22}H_{16}O_3$ *i.e.*



$O{<}\substack{C_6H_3Me\\ C_6H_3Me}{>}C{<}\substack{C_6H_4\\ O}{>}CO$. [246°]. From *p*-cresol, phthalic anhydride and H_2SO_4 at 160°. Excess of *p*-cresol is removed by steam, and the residue washed with boiling dilute KHO (Drewsen, *A.* 212, 340). Plates or prisms (from alcohol). Sol. alcohol, ether, and benzene; v. sol. $CHCl_3$; insol. ligroïn, KHO and weak acids. Conc. H_2SO_4 gives a green fluorescence. Sublimes unchanged. Reduced by zinc-dust and AcOH to the phthalin anhydride. Fused with KHO it yields di-oxy-di-methyl benzophenone. [105°]. Heating with conc. H_2SO_4 yields methyl-*erythro*-oxy-anthraquinone.

p-**Cresol phthalin anhydride** $C_{22}H_{18}O_3$ *i.e.*

$O\langle\begin{matrix}C_6H_3Me\\C_6H_3Me\end{matrix}\rangle CH.C_6H_4.CO_2H$. [210°]. From the preceding by reduction with zinc-dust and AcOH; crystallises from $CHCl_3$. V. sol. alcohol, benzene, ether, and acetic acid. Sol. conc. H_2SO_4 forming a brown solution (Drewsen, *A.* 212, 340).

o-**CRESOL SULPHONIC ACID** $C_7H_8SO_4$ *i.e.* $C_6H_3Me(OH)(SO_3H)$ [1:2:4]. From *o*-toluidine sulphonic acid by displacing NH_2 by OH through the diazo- reaction (Hayduck, *A.* 172, 204; 174, 345). Formed also in small quantity by sulphonating *o*-cresol in the cold. At high temperatures it is the only product of this sulphonation (Engelhardt a. Latschinoff, *Z.* 1869, 621; Hantke, *B.* 20, 3209). Does not crystallise. Potash-fusion converts it into salicylic acid, together with small quantities of (1,2,4)-di-oxy-benzoic acid.

Salts.—$BaA'_2$1½aq: extremely soluble aggregates of monoclinic prisms (Hayduck).—BaA'_2aq (E. a. L.).—BaA'_2: amorphous (Hantke).—KA' ¼aq: short needles (from dilute alcohol).

Methyl derivative $C_6H_3Me(OMe)(SO_3H)$. Formed by boiling *o*-diazo-toluene sulphonic acid with MeOH. Syrup.—BaA'_2 2aq: small laminæ.

Ethyl derivative $C_6H_3Me(OEt)SO_3H$. Formed by boiling *p*-diazo-toluene sulphonic acid with alcohol (Paysan, *A.* 221, 214, 363; Hayduck, *A.* 172, 215).—KA'aq.—$BaA'_2$2aq (P.).—$BaA'_2$3aq (H.).—$PbA'_2$3aq. The **amide** $C_6H_3Me(OEt).SO_2NH_2$ crystallises in laminæ [137°]; the **chloride** is an oil.

o-**Cresol sulphonic acid** $C_6H_3Me(OH).SO_3H$ [1:2:5]. From the corresponding toluidine sulphonic acid by boiling the diazo- salt with water (Nevile a. Winther, *C. J.* 37, 631). The chief product of the sulphonation of *o*-cresol in the cold (Hantke, *B.* 20, 3209). Very deliquescent needles.

Reactions.—1. At 140° it is split up by water into *o*-cresol and H_2SO_4.—2. HNO_3 (1 part) with water (2 or 3 parts) converts it into di-nitro-*o*-cresol, [86°].—3. Potash-fusion gives salicylic acid and very small quantities of a di-oxy-benzoic acid which is turned blue by Fe_2Cl_6.

Salts.—$BaA'_2$2½aq (Gerver, *A.* 169, 386). Needles (from dilute alcohol). Gives a violet colour with Fe_2Cl_6.—BaA'_2: large sparingly soluble plates (Hantke). KA': very soluble pearly plates (H.).—$CuA'_2$5aq: tables.—$PbA'_2$2½aq (G.). Small needles.

Ethyl derivative $C_6H_3Me(OEt)(SO_3H)$ [1:2:5].—From $C_6H_3Me(NH_2)SO_3H$, by heating its diazo- derivative with alcohol (Foth, *A.* 230, 306).—$BaA'_2$4aq.

m-**Cresol sulphonic acid** $C_6H_3Me(OH)(SO_3H)$ [1:3:6]. [118°]. From *m*-cresol and H_2SO_4 at 110° (Claus a. Krauss, *B.* 20, 3089; *cf.* Engelhardt a. Latschinoff, *Z.* 1869, 622; Nölting a. Salis, *B.* 15, 1862). Plates (containing 2aq) [75°] (from dilute H_2SO_4) or (containing 1½aq) [96°] (from conc. H_2SO_4). V. sol. water, alcohol, ether, and benzene. Gives a violet colour with Fe_2Cl_6. CrO_3 gives toluquinone.—KA'2½aq: stellate group of needles with fatty lustre.—$CuA'_2$3aq: tufts of pale-green prisms.—BaA'_2aq: nodules.—$BaC_7H_6SO_4$2aq.

p-**Cresol sulphonic acid** $C_6H_3Me(OH)(SO_3H)$ [1:4:2]. [188°]. From *p*-toluidine sulphonic acid by the diazo- reaction (Jenssen, *A.* 172, 237). Long needles (containing 5aq) [99°]. V. sol. water, alcohol, and ether. Hydrolysed by passing steam through its solution in dilute H_2SO_4 boiling above 120° (Armstrong a. Miller, *C. J.* 45, 148).—BaA'_2: amorphous, v. e. sol. water. Its solution is coloured violet by Fe_2Cl_6.

Methyl derivative $C_6H_3Me(OMe)SO_3H$. From the diazo- derivative of toluidine sulphinic acid by gently warming with methyl alcohol (Limpricht a. Heffter, *A.* 221, 352). Its **amide** crystallises in prisms [150°]; its **chloride** is an oil.—BaA'_2.—KA'.

Ethyl derivative $C_6H_3Me(OEt)(SO_3H)$. Prepared as above, using ethyl alcohol. Formed also by warming diazo-toluene sulphonic acid with alcohol (Remsen a. Palmer, *Am.* 8, 245).—BaA'_2 3½aq.—KA'. The **amide** $C_6H_3Me(OEt)SO_2NH_2$ [136°] (L. a. H.); [144°] (R. a. P.) crystallises in needles. The **chloride** is an oil.

p-**Cresol sulphonic acid** $C_6H_3Me(OH)(SO_3H)$ [1:4:3]. From *p*-cresol and fuming H_2SO_4. Also from the corresponding *p*-toluidine sulphonic acid by the diazo- reaction (Engelhardt a. Latschinoff, *Z.* 1869, 619; Pechmann, *A.* 173, 203). Syrup. Fe_2Cl_6 colours its solution blue. Potash-fusion gives *p*-oxy-benzoic acid.—KA'2aq: laminæ.—BaA'_2: tables. S. 7 at 17° (Baumann, *H.* 4, 313).—$BaC_7H_6SO_4$2aq. V. sl. sol. water.—$PbA'_2$3aq.—$PbA'_2$1½aq: laminæ (from alcohol).

Cresol sulphonic acid $C_6H_3Me(OH)(SO_3H)$ [1:?2:*x*]. Formed by fusing toluene di-sulphonic acid with KOH (Brunner, *Sitz. W.* [2] 78, 665). Feathery groups of crystals (containing ½aq at 100°) [81°]. Hygroscopic. V. sol. alcohol and ether.—$NaA'_2$2aq.—KA'2aq: prisms [c. 228°].—BaA'_2aq. Its solution is turned blue by Fe_2Cl_6.—$CaA'_2$1½aq.—$PbA'_2$3aq.—$CuA'_2$8aq.—$ZnA'_2$10½aq.

Cresol sulphonic acids have been obtained by sulphonating cresols by Duclos (*A.* 109, 138), and by Armstrong a. Field (*B.* 6, 974), but not sufficiently characterised.

p-**Cresol** *exo*-**sulphonic acid** $C_6H_4(OH).CH_2SO_3H$ [1:4]. From $C_6H_4(NH_2).CH_2SO_3H$ by diazo- reaction (Mohr, *A.* 221, 221). Deliquescent needles; v. sol. alcohol. The aqueous solution is turned bluish-violet by Fe_2Cl_6.—KA', ½aq.—BaA'_2 7½aq.

Ethyl derivative $C_6H_4(OEt).CH_2.SO_3H$. Prepared by decomposing the diazo- derivative of $C_6H_4(NH_2).CH_2.SO_3H$ by boiling with alcohol.—BaA'_2 2aq.

o-**Cresol disulphonic acid** $C_6H_2Me(OH)(SO_3H)_2$ [1:2:3:5]. From *o*-toluidine disulphonic acid by diazo- reaction (Limpricht, *B.* 18, 2176; H. Hasse, *A.* 230, 293). Tables or needles. V. sol. water and alcohol.—K_2A'' 1½aq: very soluble needles.—BaA'' 3½aq: small needles.

Ethyl derivative $C_6H_2Me(OEt)(SO_3H)_2$. From the diazo- derivative of *o*-toluidine disulphonic acid by boiling with alcohol under an extra pressure of 400 mm.—BaA'' 2½aq.

m-**Cresol disulphonic acid** $C_6H_2Me(OH)(SO_3H)_2$. From *m*-cresol (1 pt.) and

H_2SO_4 (5 pts.) at 130° (Claus a. Krauss, *B.* 20, 3089). V. sol. water and alcohol, m. sol. ether and benzene.—KA′ 3aq : plates.—BaA'_2 ½aq.

p-**Cresol disulphonic acid** $C_6H_2Me(OH)(SO_3H)_2$ [1:4:3:2or6]. From *p*-toluidine di-sulphonic acid by diazo- reaction (Limpricht, *B.* 18, 2178; E. Richter, *A.* 230, 322). Needles. V. e. sol. water and alcohol.—BaA″ 4aq : needles.—K_2A'' ½aq ? : tables.—PbA″ 3aq : v. sol. water.

p-**Cresol disulphonic acid** $C_6H_2Me(OH)(SO_3H)_2$ [1:4:3:5]. From *p*-cresol sulphonic acid and fuming H_2SO_4 (Engelhardt a. Latschinoff, *Z.* 1869, 620).—K_2A'' 3aq : crystals, v. e. sol. water.—BaA″ 2½aq : needles, sl. sol. water.

m-**Cresol trisulphonic acid** $C_6HMe(OH)(SO_3H)_3$. From *m*-cresol, fuming H_2SO_4, and P_2O_5 at 180° (Claus a. Krauss, *B.* 20, 3089). The Ba salt is v. sol. water.

CRESORCELLIC ACID *v.* (5:3:2:1)-DI-OXY-*o*-TOLUIC ACID.

CRESORCIN *v.* DI-OXY-TOLUENE.

CRESORCIN-CARBOXYLIC ACID *v.* DI-OXY-TOLUIC ACID.

CRESOTIC ACID *v.* OXY-TOLUIC ACID.

CRESS OIL. The volatile oil of garden-cress (*Lepidium sativum*) consists to the extent of 75 p.c. of phenyl-acetonitrile (benzyl cyanide) (Hofmann, *B.* 7, 1293). The volatile oil of water-cress (*Nasturtium officinalis*) consists of phenyl-propionitrile (Hofmann, *B.* 7, 520).

CRESYL COMPOUNDS *v.* TOLYL COMPOUNDS.

CROCETIN $C_{34}H_{46}O_9$. Formed by the action of dilute acids on crocin, a sugar (crocose) being the correlative product (Kayser, *B.* 17, 2231). Red powder. V. sol. alcohol and ether, nearly insol. water. Dissolves in alkalis with a yellow colour. Like crocin it dissolves in H_2SO_4 with a blue colour, which slowly becomes violet, red, and finally brown. Stuffs mordanted with stannous chloride acquire, by boiling in a solution of crocetin (from Gardenia), a dingy greenish-yellow colour, which by treatment with ammoniacal water is converted into a brilliant yellow colour, unaltered by light and air. The yellow robes of the Chinese mandarins are dyed with the fruit of the *Gardenia.*

CROCIN (*the colouring matter of saffron*) $C_{10}H_{70}O_{28}$. Appears to be identical with the colouring matter of Chinese yellow pods (*Gardenia grandiflora*) (Rochleder, *J. pr.* 56, 68). Yellow powder. V. sol. water and dilute alcohol, sl. sol. absolute alcohol, nearly insol. ether.

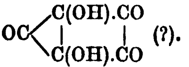
Preparation.—The saffron, which has been previously extracted with ether, is soaked in cold water, the colouring-matter is removed from the aqueous solution by animal charcoal, and after drying is extracted from the charcoal by means of 90 p.c. alcohol.

Reactions.—It dissolves in H_2SO_4 with a deep blue colour, which gradually becomes violet, then red, and finally brown. HNO_3 also produces a blue colouration, which almost instantaneously passes into brown. By dilute acids it is split up into crocetin $C_{34}H_{46}O_9$ and a sugar (crocose) $C_6H_{12}O_6$ (Kayser, *B.* 17, 2228).

CROCONAMIC ACID $C_5H_3NO_4$ *i.e.* $C_5O_3(OH)(NH_2)$, or more probably $C_5O_2(NH)(OH)_2$. *Imido-croconic acid.*—The ammonium salt is formed by heating the di-anilide of croconic acid with aqueous NH_3. Mono-basic acid.

Salts.—$A'NH_4$: red prisms with bluish reflex. A′Ag *x*aq : yellow needles.—A'_2Ba 3aq : sparingly soluble small yellow needles.—BaC_5HNO_4 4aq : sparingly soluble yellow plates (Nietzki a. Benckiser, *B.* 19, 773; 21, 1856).

CROCONIC ACID $C_5H_2O_5$ or



$$\mathrm{OC}\left\langle\begin{array}{l}\mathrm{C(OH).CO}\\ \;\;|\qquad\quad\;\;|\\ \mathrm{C(OH).CO}\end{array}\right. (?).$$

Formation.—1. From the black-residues obtained in the preparation of potassium by Brunner's method (Gmelin, *P.* 4, 37; *A.* 37, 58; Liebig, *A.* 11, 182; *P.* 33, 90; Heller, *J. pr.* 12, 230; *A.* 24, 1; 34, 232; Will, *A.* 118, 177). When CO is passed over melted potassium and the product is treated with water, a red salt, **potassium rhodizonate**, is formed. A solution of this salt changes on standing exposed to air to potassium croconate. Excess of alkali converts rhodizonic acid into croconic acid dihydride, which appears to be an intermediate body in the formation of croconic acid from rhodizonic acid (Nietzki, *B.* 20, 1617).—2. By heating benzene-tri-quinone C_6O_6 to 100°, or by boiling it with water, CO_2 being evolved.—3. By exposing an alkaline solution of tetra-oxy-quinone $C_6(OH)_4O_2$ to the air, oxalic acid being formed simultaneously.—4. By evaporating hexa-oxy-benzene $C_6(OH)_6$ with dilute KOH in an open dish (Nietzki a. Benckiser, *B.* 18, 509).

Preparation.—By boiling the hydrochloride of diamidotetraoxybenzene $C_6(NH_2)_2(OH)_4$ (1 pt.) with K_2CO_3 (4 pts.) precipitated MnO_2 (3 pts.) and water (60 pts.) for ½ hour; on adding $BaCl_2$ to the filtrate acidified with HCl the sparingly soluble barium croconate separates in golden-yellow plates; the yield is 70 p.c. of the theoretical (Nietzki a. Benckiser, *B.* 19, 293).

Properties.—Sulphur-yellow plates or grains (containing 3aq). V. sol. water, sol. dilute alcohol. Di-basic acid. Forms a sparingly soluble red crystalline anilide. Heated with NH_3 it gives the tri-imide of leuconic acid. With hydroxylamine it gives the penta-oxim of leuconic acid $C_5(NOH)_5$. By H_2S it is converted into thio-croconic acid $C_5H_2O_4S$. It is reduced by $SnCl_2$, SO_2, or zinc-dust to the colourless hydro-croconic acid $C_5H_4O_5$, which is readily reoxidised to croconic acid. By heating potassium croconate with HI it is reduced to 'croconic-acid-hydride' ($C_{10}H_6O_{10}$?), whose salts are deep coloured; by further reduction it gives a colourless substance which is readily reoxidised to the hydride. Croconic acid is oxidised by HNO_3 to leuconic acid C_5O_5.

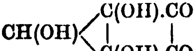
Salts.—K_2A'' : long dark-yellow needles (N. a. B.).—K_2A'' 2aq : orange needles (G.).—HKA″ : brownish-yellow needles with violet reflex.—NaKA″ *x*aq : yellow rhombic plates, become red on drying.—CaA″ 3aq : yellow powder (W.).—BaA″ 1½aq : lemon-yellow powder, insol. water, v. sl. sol. HClAq.—PbA″ 2aq : lemon-yellow pp., insol. water. — CuA″ 3aq : sparingly soluble orange needles with blue reflex.—Ag_2A'' : orange pp.

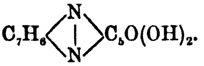
Aniline salt $A''(NH_3Ph)_2$: yellow plates, m. sol. water.

Di-anilide $C_5(HO)_2O(NPh)_2$: slender red needles. Formed by heating the aniline salt with alcohol. **V. sl. sol. all solvents but aniline. Dissolves in aqueous alkalis, and on heating the solution croconic acid and aniline are regenerated.** Heated with aqueous NH_3 it is converted into croconamic acid $C_5H_3NO_4$ (Nietzki a. Benckiser, *B.* 19, 772).

Mono-phenylhydrazide $C_5(OH)_2O_2(N_2HPh)$: [above 300°]; yellow needles; v. sol. alcohol, insol. water. Di-basic acid.– K_2A'': nearly black coppery needles, v. sol. water with a brown colour.

Tolylene-o-diamide v. CROCONIC-DI-TOLUQUINOXALINE.

'Croconic-acid-hydride' $C_5H_4O_5$ or $C_{10}H_6O_{10}$ *i.e.*  $CH(OH)<\begin{matrix}C(OH).CO\\ | \qquad\quad | \\ C(OH).CO\end{matrix}$ (?). *The 'hydrocroconic acid' of Lerch* (*A.* 124, 20). Formed by heating potassium croconate with HI. Its salts are dark-coloured. By further reduction it is converted into a colourless substance, which is readily reoxidised to the hydride.—$C_5H_2O_5Ba$ 2aq or $C_{10}H_2O_{10}Ba_2$ 4aq: deep orange crystalline powder or amorphous flocculent pp.—$PbC_5H_2O_5$: red pp. (Nietzki a. Benckiser, *B.* 19, 297).

CROCONIC-TOLUQUINOXALINE $C_{12}H_8N_2O_3$ *i.e.*  $C_7H_6<\begin{matrix}N\\ | \\ N\end{matrix}>C_5O(OH)_2$. *Croconic-acid-tolylene-o-diamide.* Formed by mixing a cold aqueous solution of croconic acid with a salt of tolylene-*o*-diamine. Fine needles, with green reflex. Sol. alcohol with a brown colour, insol. water. Dibasic acid. — $A''K_2$: black metallic needles (Nietzki a. Benckiser, *B.* 19, 776).

CROCOSE (*saffron-sugar*) $C_6H_{12}O_6$. Trimetric crystals. Sweet taste. Dextrorotatory. Its reducing power is half that of dextrose. Formed, together with crocetin, by the action of dilute acids on crocin (Kayser, *B.* 17, 2232; *cf.* Rochleder a. Mayer, *J.* 1858, 476; *Sitz. W.* 29, 3).

CROSSOPTERINE. An amorphous alkaloid in the bark of *Crossopterix Kotschyana* (Hesse, *B.* 11, 1546).

CROTACONIC ACID $C_3H_4(CO_2H)_2$. [119°]. Solidifies at 90°. From cyano-crotonic acid which changes spontaneously into acid ammonic crotaconate (Claus, *A.* 191, 74; *B.* 10, 822).

Properties.—Crystals. Sol. water, alcohol, and ether. At 140° it decomposes, giving off CO_2 (difference from itaconic, citraconic, &c.). Combines with HBr forming an acid $C_3H_5Br(CO_2H)_2$ [141°].

Salts.—$(NH_4)HA''$. — KHA'' 2aq.—K_2A''aq. —PbA''.—Ag_2A''.

Dimethyl ether Me_2A''. S.G. $\frac{15}{}$ 1·14. Sol. alcohol and ether.

Isomerides: CITRACONIC, ITACONIC, MESACONIC, and ETHYLIDENE-MALONIC, ACIDS.

CROTONIC ACID $C_4H_6O_2$ *i.e.* $CH_3.CH:CH.CO_2H$. Mol. w. 86. [72°]. (185° cor.). S. 8 at 19°. R_∞ 35·71 in a 4·12 p.c. aqueous solution (Kanonnikoff).

Occurrence.—In crude wood vinegar (Krämer a. Grodzki, *B.* 11, 1359). Its name is derived from croton oil, from which it was erroneously supposed to be formed by saponification (Pelletier a. Caventou, *J. Ph.* 4, 289; 11, 110; Schlippe, *A.* 105, 1; Geuther, *Z.* [2] 5, 270).

Preparation.—1. By oxidation of crotonic aldehyde (from acetic aldehyde) in the air or by moist Ag_2O (Kekulé, *B.* 3, 604; *Z.* [2] 6, 705).—2. From allyl cyanide (*v.* vol. i. p. 136) obtained from mustard oil (Will a. Körner, *A.* 125, 273).—3. By distillation of (*β*)-oxy-butyric acid (Wislicenus, *Z.* 1869, 325).—4. By boiling *a*-bromo-butyric ether with alcoholic KOH (Hell a. Lauber, *B.* 7, 560).—5. From isocrotonic acid by intramolecular change brought about by heating to 175° (Hemilian, *A.* 174, 322).—6. From malonic acid (1 mol.), paraldehyde (1 mol.), and excess of glacial acetic acid at 100° (Komnenos, *A.* 218, 149). The yield is good (50 p.c.).—7. By heating pyruvic acid (1 pt.) with Ac_2O (5 pts.) and NaOAc (5 pts.) at 170° (Homolka, *B.* 18, 987).—8. By reduction of aceto-acetic ether with sodium-amalgam (Beilstein a. Wiegand, *B.* 18, 482).

Properties.—Trimetric plates (by sublimation) or monoclinic crystals (from water); $a{:}b{:}c = 1{:}1·8065{:}1·5125$; $\beta = 131°$. M. sol. hot ligroin.

Reactions.—1. *Potash-fusion* forms only acetic acid.—2. Not reduced to butyric acid by *sodium amalgam* (Korner, *J.* 1866, 318; *A.* 137, 233; *cf.* Bulk, *A.* 139, 62).—3. Br gives *aβ*-di-bromo-butyric acid.—4. Conc. HBr at 100° gives *a*- and a little *β*- bromo-butyric acid.—5. HOCl gives chloro-oxy-butyric acid.—6. Conc. HNO_3 gives acetic and oxalic acids.—7. *Chromic acid mixture* gives aldehyde and acetic acid (Kekulé, *A.* 162, 315).—8. Aqueous *ammonia* forms *a*-amido-butyric acid (Engel, *C. R.* 106, 1677).

Salts.—KA': deliquescent needles. -KHA'_2: plates (from alcohol) (Pinner, *B.* 17, 2008).—NaA'. S. (alcohol) 1·4 at 14°.—BaA'_2: easily soluble plates.—CaA'_2: v. sol. cold, sl. sol. hot, water (Beilstein a. Wiegand, *B.* 18, 482).—PbA'_2: stellate groups of needles.–ZnA'_2 2aq (Alberti, *B.* 9, 1194).—AgA': curdy pp.

Methyl ether MeA'. (121°). S.G. $\frac{4}{}$ ·9806. $\mu_D = 1·4138$ (Kahlbaum, *B.* 12, 344).

Ethyl ether EtA'. (139° cor.). $\mu_D = 1·424$. R_∞ 50·45 (Brühl, *A.* 235, 8; *B.* 14, 2798). S.G. $\frac{15}{15}$ ·9268; $\frac{25}{25}$ ·9185. M.M. 7·589 at 24·4° (Perkin, *C. J.* 45, 537).

Amide. Syrup; v. sol. water (B. a. W.). A crystalline amide [c. 151°] was obtained by Pinner (*B.* 17, 2008) by exposing to the air the hydrochloride of *β*-chloro-butyrimido-ether $CH_3.CHCl.CH_2.C(OEt).NH_2Cl$.

Iso-crotonic acid $C_4H_6O_2$ *i.e.* $CH_2:CH.CH_2.CO_2H$ (?). *Quartenylic acid.* (172° cor.). S.G. $\frac{25}{}$ 1·018. Occurs in crude wood vinegar (Grodzki a. Krämer, *B.* 11, 1359).

Preparation.—Aceto-acetic ether is treated with PCl_5 and the product poured into water. The two chloro-crotonic acids formed are distilled with steam. The chloro-iso-crotonic acid alone passes over. It is reduced by sodium amalgam, and the iso-crotonic acid is extracted by ether. On evaporation this leaves iso-crotonic acid as a syrup.

Properties.—Liquid, smelling like butyric acid; miscible with water. At 175° it changes to the preceding isomeride (Hemilian, *A.* 174, 322).

Reactions.—1. *Bromine* acting on a solution of iso-crotonic acid dissolved in CS_2 produces the dibromide of ordinary solid crotonic acid (*v.* DI-BROMO-BUTYRIC ACID) (Kolbe, *J. pr.* [2] 25, 397).—2. *Potash-fusion* gives only acetic acid.—3. *Sodium amalgam* has no action.

Salts.—CaA′$_2$2aq: very soluble needles.—BaA′$_2$2aq: small crystals, v. e. sol. water.—PbA′$_2$aq. [68°].—AgA′.

Ethyl ether EtA. (136°). S.G. $\underline{19}$ ·927 (Geuther, *Z.* 1871, 243).

Isomeride of crotonic acid $C_4H_6O_2$. [19°]. (181°). From vinaconic acid (*q.v.*) by distillation (Röder, *A.* 227, 24).

Salts.—CaA′$_2$ 6aq.—BaA′$_2$2aq.—AgA′.

Constitution.—From its formation, from $CH_2{:}CH.CH(CO_2H)_2$ it should be vinyl-acetic acid, $CH_2{:}CH.CH_2.CO_2H$, a formula, attributed, without sufficient reason, to isocrotonic acid.

Another isomeride of crotonic acid *v.* METHACRYLIC ACID.

Dibromide of crotonic acid *v.* DI-BROMO-BUTYRIC ACID.

Derivatives of crotonic acid *v.* BROMO-CROTONIC ACIDS and CHLORO-CROTONIC ACIDS.

CROTONIC ALDEHYDE C_4H_6O *i.e.* $CH_3.CH{:}CH.CHO$. Mol. w. 70. (105°). S.G. $\underline{0}$ 1·033.

Formation.—1. By heating aldehyde with $ZnCl_2$ and a little water to 100°, aldol being first formed: $2CH_3.CHO = CH_3.CH(OH).CH_2.CHO = CH_3.CH{:}CH.CHO + H_2O$. Other dehydrating agents may be used (Lieben, *A. Suppl.* 1, 117; Kekulé, *Z.* [2] 5, 572; *A.* 162, 92; Bauer, *A.* 117, 141; Lieben a. Zeisel, *M.* 1, 820). Hence it occurs in crude spirit (Krämer a. Pinner, *B.* 3, 75).—2. By the distillation of aldol (Wurtz, *C. R.* 87, 45).—3. From vinyl bromide by successive treatment with H_2SO_4 and water (Zeisel, *A.* 191, 371).—4. From acetylene by successive treatment with H_2SO_4 and water (Lagermarck a. Eltekoff, *B.* 10, 637).

Preparation.—Paraldehyde (1 pt.), water (1 pt.), and conc. HClAq (2 pts.) are kept at 25° for 5 days. The liquid is then neutralised with Na_2CO_3, the ppd. dialdane is filtered off, and the filtrate extracted with ether. The ethereal extract is distilled under reduced pressure, and the crude aldol ($\frac{1}{2}$ pt.) (85° to 120° at 200 mm.) is split up into water and crotonic aldehyde ($\frac{1}{3}$ pt.) by distillation under ordinary pressure (Newbury, *C. R.* 92, 196; *Am.* 5, 113).

Properties.—Pungent liquid; m. sol. water. Oxidised in the air or by Ag_2O to crotonic acid. It forms a crystalline combination with $NaHSO_3$, m. sol. water, whence Na_2CO_3 does not liberate the aldehyde (Lieben a. Zeisel, *M.* 1, 818).

Reactions.—1. PCl_5 gives di-chloro-butylene (126°).—2. By saturation with HCl in the cold it is converted into β-chloro-butyric aldehyde [97°].—3. Br gives oily αβ-di-bromo-butyric aldehyde (L. a. Z.).—4. Cl forms αβ-di-chloro-butyric aldehyde, and finally αβ-di-chloro-butyryl chloride (Zeisel, *M.* 7, 359).—5. *Iron* and *acetic acid* reduce it to butyric aldehyde, butenyl alcohol, and *n*-butyl alcohol (L. a. Z.).—6. Ac_2O gives the di-acetyl derivative of crotonic orthaldehyde $CH_3.CH{:}CH.CH(OAc)_2$ (205°–210°). S.G. $\underline{14}$ 1·05 (Lagermarck a. Eltekoff, *J. R.* 11, 79).—7. Dilute HCl at 0° forms, by hydration, a little aldol, paraldol, and dialdane (Wurtz, *C. R.* 97, 1169).—8. *Ammonia* forms tri-crotonylene-amine $C_{12}H_{24}N_4$. At −20° ammonia passed into an ethereal solution of the aldehyde forms $C_8H_{16}N_2O$ (Combes, *C. R.* 96, 1862).—9. Crotonic aldehyde (1 pt.) treated with *aldehyde* (2 pts.) and $ZnCl_2$ at 100° forms an aldehyde C_6H_8O (172°) Kekulé, *A.* 162, 105).—10. By heating with HCN and saponifying the product pentinoic acid $CH_2{:}CH.CH{:}CH.CO_2H$ is formed (Lobry de Bruyn, *Bl.* [2] 42, 159).

Derivative $CH_3.CH{:}CH.CHCl(OEt)$. (134°). From di-chloro-butylene and alcoholic KOH (Kekulé, *A.* 162, 99).

CROTONITRILE *v.* ALLYL CYANIDE.

CROTON OIL. A fatty oil contained to the amount of 50 p.c. in the seeds of *Croton Tiglium*, a euphorbiaceous plant. It is purgative, and inflames the skin (Schlippe, *A.* 105, 1; Mayer. *N. Jahr. pr. Pharm.* 10, 318; Geuther a. Fröhlich, *Z.* [2] 6, 26, 549). It contains glycerides of formic, acetic, isobutyric, isovaleric (isobutyl-formic) and tiglic acids (E. Schmidt a. J. Berendes, *A.* 191, 94; *B.* 10, 835; *Ar. Ph.* [3] 13, 213). The nature of the purgative principle has not been satisfactorily made out (Senier, *Ph.* [3] 14, 446; Kobert, *Chem. Zeit.* 11, 416).

CROTONYL ALCOHOL *v.* BUTENYL ALCOHOL, vol. i. p. 639.

CROTONYLENE *v.* BUTINENE.

TRI-CROTONYLENE-AMINE $C_{12}H_{24}N_4$. (c. 190°) at 40 mm. Formed by heating aldol with excess of aqueous NH_3 at 160°; or from crotonic aldehyde and NH_3 at 100° (Wurtz, *C. R.* 88, 1154). Efflorescent prisms (containing 6aq); sl. sol. cold water, v. sol. alcohol. HCl at 150° resinifies it.

Salts.—Crystallise readily from acid solutions. —B′3HCl: hexagonal prisms.—B′3HNO$_3$: hexagonal prisms.—$B'H_3Cl_3(PtCl_4)_2$.—$B'_2H_8Cl_8(PtCl_4)_3$.—$B'H_4Cl_4AuCl_3$.—$B'H_3Cl_3AuCl_3$2aq.—$B'_2H_8Cl_8(AuCl_3)_5$.

CROTONYLENE GLYCOL *v.* ERYTHRITE and DI-OXY-BUTYLENE.

CROTYL ALCOHOL *v.* BUTENYL ALCOHOL.

CROTYLAMINE $C_4H_7NH_2$. (75°–80°). Prepared by the action of alcoholic NH_3 on isobutylene bromide. Liquid (Hofmann, *B.* 7, 514; 12, 992).—$(B'HCl)_2PtCl_4$. Yellow scales.

ISO-CROTYL BROMIDE *v.* BROMO-BUTYLENE.

ISO-CROTYL CHLORIDE *v.* CHLORO-ISOBUTYLENE.

CROTYL IODIDE *v.* IODO-BUTYLENE.

CROTYL THIOCARBIMIDE C_4H_7N CS. (179°). From crotylamine (Hofmann, *B.* 7, 516). Pungent liquid.

CROTYL-THIO-UREA $C_4H_7NH.CS.NH_2$. [85°]. From the preceding and NH_3(H). Crystalline.

CRYPTIDINE $C_{11}H_{11}N$. (274°). A homologue of quinoline occurring in coal tar (Greville Williams, *Chem. Gaz.* 1856, 283).

Cryptidine $C_{11}H_{11}N$. (270°). Prepared by the dry distillation of xylidine-acroleïn (Leeds, *A. C. J.* 5, 2). Reddish-yellow oil. Disagreeable odour. Bitter taste.—B′HCl: fine thin tabular crystals.—$B'H_2PtCl_6$: fine yellow crystals. Sol. water, insol. alcohol.

CRYPTOPHANIC ACID $C_5H_9NO_5$. An acid said to occur in normal human urine (Thudichum, *C. J.* 23, 116; 34, 81). The urine is evaporated to one-fourth of its bulk and Fe_2Cl_6 added. The pp. contains the iron salts of cryptophanic, paraphanic, hippuric, and benzoic acids. It may be decomposed by baryta. Amorphous gum, v. e. sol. water.—PbA″.—CaA″.

CRYPTOPINE $C_{21}H_{23}NO_5$. [217°]. S. (alcohol) ·08 (Smith). S.G. 1·35 (Schröder *B.* 13, 1075). A base occurring in very small quantity in opium (T. a. H. Smith, *Ph.* [2] 8, 595, 716; Hesse, *A. Suppl.* 8, 299; *A.* 176, 200; Kauder, *Ph.* [3] 18, 250). Ppd. by adding NaOH to the mother-liquor, from which codeine, narceine, thebaïne, and papaverine have been separated. Six-sided prisms (from alcohol); when freshly ppd. it is soluble in ether, but it slowly separates from the solution. Sl. sol. boiling alcohol, v. sl. sol. benzene and ligroin, m. sol. chloroform. Dissolves in excess of KOHAq. Inactive to light. Conc. (impure) H_2SO_4 gives a blue colour turned orange by KNO_3. Fe_2Cl_6 gives no colour. Not decomposed by HCl.

Salts.—Separate from aqueous solution as jellies, but subsequently become crystalline.—$B'HCl$ 6aq: soft mass of crystals (from alcohol).—$B'HCl$ 5aq. — $B'_2H_2PtCl_6$ 6aq. — $B'_2H_2Cr_2O_7$.— $B'H_2C_2O_4$. S. ·3 at 12°.—$B'C_4H_6O_6$ 4aq. S. ·15 at 10°. - $B'C_6H_2(NO_2)_3OH$ aq.

Meconate $B'_2C_7H_4O_7$ 10aq: sl. sol. boiling water.

Nitro-cryptopine $C_{21}H_{22}(NO_2)NO_5$. [185°]. From cryptopine and HNO_3 (S.G. 1·06) at 55°. Dark-yellow crystalline powder. Insol. water and KOHAq. Conc. H_2SO_4 dissolves it with blood-red colour. -$B'HCl$ 3aq.—$B'_2H_2PtCl_6$ 10aq. —$B'HNO_3$. - **Oxalates** $B'_2H_2C_2O_4$ 12aq. S. 6·8 at 16° and $B'H_2C_2O_4$ 3aq.

CRYSTALLIN *v.* PROTEÏDS.

CRYSTALLISATION.—The examination of a crystal and the determination of its form and properties may serve as a means of recognising and defining any given body. But besides this practical application, the examination may help to find an answer to the question: What is the connexion between the chemical constitution and the crystalline form of bodies?

The complete examination of the form and properties of a crystalline substance may demand a thorough knowledge of crystallography, and also skill in the use of complicated and costly instruments; but a general knowledge of the principles of the subject, and of the use of a geological microscope, such as ought to be found in every laboratory, will very often enable the chemist approximately to determine the form of a substance, the identity or non-identity of two samples, or the homogeneous character of his preparations. The following account may serve as a general view of the subject, or as an introduction to a more complete study; it is necessarily incomplete, and for further details special books must be consulted, such as Groth's *Physikalische Krystallographie*; current literature being found in the *Zeitschrift für Krystallographie*, and the different mineralogical journals.

A crystal may be described as a solid homogeneous body bounded by plane faces that are arranged around the body in a certain regular manner, which is constant for each chemical compound. Neither the number of faces that bound a crystal, nor the shapes of these faces, are constant and characteristic, since both may vary considerably with very slight alterations of external conditions at the time of crystallisation; but the regularity, or the symmetry which all the faces bear to each other, and the manner in which the faces occur in groups or sets or '*forms*,' is constant and characteristic.

Single or Simple crystalline form.—That all the faces of a crystal do not belong to the same form is often strikingly evident by a difference in colour, as in many of the platinocyanides, or in the condition of the faces, some of which are smooth and lustrous, while others are dull or streaked with numerous fine lines, or are rough with little pittings, or appear to be made up of numerous scales, and then show a pearly lustre; such differences are to be noticed on crystals of magnesium sulphate, quartz, salt, alum, potassium ferrocyanide, potassium chlorate, gypsum, copper sulphate, &c. The same fact is often also to be noticed in another way, viz. by the appearance of splits or cleavage planes that run parallel to certain faces but not to others, as in calcite and potassium ferrocyanide; often where such are not manifest the crystal may be easily split or cleaved parallel to certain faces but not to others, as with gypsum, cane sugar, magnesium sulphate, &c. Differences in the forms of the faces of crystals are often shown by the way in which the crystal during its growth has inclosed foreign substances, as bubbles of liquid or gas, or fragments of solid substances that were suspended in the solution, viz. the inclosures are distributed in lines or planes parallel to certain edges or planes of the crystal, but not to others. In examining a crystal all such observations are of the greatest service, as they at once give a means of classifying the may-be numerous faces into their proper sets or forms.

A crystal may be completely bounded by only one set of faces, *e.g.* a cube of rock salt; but there are several crystalline forms that are not capable of inclosing space, as the various prisms and pinacoids, or basal planes, and such forms necessarily never occur alone. The minimum number of crystalline forms that may occur on a crystal is limited only by the condition that they must completely inclose the crystal; the maximum number is unlimited; but however many there may be, all are correlated by an empirical law, known as the *rationality of indices*, and the symmetry of faces constituting each individual form is the same.

This last statement, though strictly true, is apparently not so in several cases, as certain forms show externally a geometrical symmetry apparently other than that which belongs to their internal structure; thus both salt and iron pyrites crystals often exhibit no other form than the cube, and therefore are apparently possessed of the same kind and amount of symmetry, yet other forms that occur in these two substances show that iron pyrites is really possessed of a lower degree of symmetry than sodium chloride (*v. Hemihedral forms*, p. 283).

Symmetry of crystalline forms.—A solid figure may be symmetrical about a point, or about a plane, or a number of planes. A solid figure is *symmetrical about a point* when any number of particles on the surface being joined to the central point by straight lines, these being produced to equal distances on the other side of the centre shall exactly coincide with a series of similar particles. This kind of symmetry only demands that to every face there be a second and parallel one; it is only met with in the asymmetric (*i.e.* without symmetry) crystals, as, for instance, copper sulphate and potassium anhydrochromate.

A solid figure is *symmetrical about a plane* when from any number of particles on the surface perpendiculars being drawn to the plane and produced equal distances on the other side of the plane, the points so found shall exactly coincide with a series of similar particles; in other words, the one half is the mirrored image of the other, the mirror being the *plane of symmetry*. Thus a cube is symmetrical about the plane *a c g e*. A line perpendicular to the plane of symmetry is called an *axis of symmetry*, and about a central point in this axis the figure is also symmetrical. Thus (fig. 1), starting with *a c g e* as a plane of symmetry, and *a b f e* as any given plane, the existence of *a d h e* and *d c g h* necessarily follows, as the former is the image mirrored in the plane of symmetry, and the latter is the plane symmetrical to the first with regard to the central point; the existence of *b c g f* follows similarly from either or both of the last two faces.

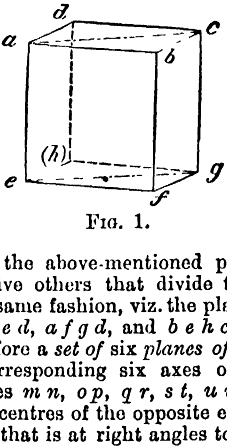


FIG. 1.

Besides the above-mentioned plane *a c g e* there are five others that divide the cube in exactly the same fashion, viz. the planes *b d h f*, *b a h g*, *c f e d*, *a f g d*, and *b e h c*, and these make therefore a *set of* six *planes of symmetry*; and the corresponding six axes of symmetry are the lines *m n*, *o p*, *q r*, *s t*, *u v*, and *w x*, joining the centres of the opposite edges (fig. 2).

A plane that is at right angles to two planes of symmetry contains two axes of symmetry, and must therefore itself be a plane of symmetry; and if, as in the case now considered, the two contained axes of symmetry are similar, then the symmetry of the new plane is of a higher order than that of the two others. The above six planes may be taken two at a time in three different ways, and thus a set of three new planes of a higher order are found; they are called *planes of principal symmetry* as distinguished from *planes of ordinary symmetry*; they are *q s r t*, *w u x v*, and *o m p n* (fig. 2), and the corresponding *axes of principal symmetry* are the lines A B, C D, and E F (fig. 3). As a plane of principal symmetry contains two, and in the hexagonal system three, exactly similar axes of symmetry, the appearance and actual position of a crystal is not changed by rotating it about the axis of principal symmetry such that first one and then another of the similar axes of ordinary symmetry come to occupy the same position. In this way a plane of principal symmetry may be most readily distinguished from a plane of ordinary symmetry.

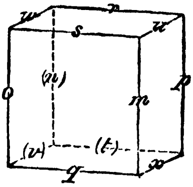


FIG. 2.

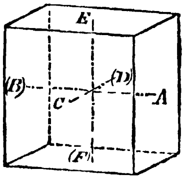


FIG. 3.

Division of crystals into classes.—A crystal can only be possessed of a set of three exactly similar axes of principal symmetry, or of one such axis, or it must be devoid of any such; and all crystals may accordingly be divided into three great classes: (1) Crystals possessed of three axes of principal symmetry must necessarily contain also a set of six axes of ordinary symmetry (as explained above in the case of the cube), and all such are said to belong to the *Regular system*. (2) Crystals possessing one axis of principal symmetry must necessarily contain axes of ordinary symmetry at right angles to the first. The number of these axes of ordinary symmetry may be either (1) a set of three inclined to each other at one-third of four right angles, with, as a necessary consequence, a second set of three, also inclined to each other at one-third of four right angles, but removed from the first set by one-sixth of four right angles, or (2) a set of two at right angles to each other, with, as a necessary consequence, a second set of two also at right angles to each other, but removed from the first set by half a right angle. Crystals satisfying the first set of conditions are said to belong to the *Hexagonal system*, and those satisfying the second set to the *Quadratic system*. (3) Crystals destitute of any axis of principal symmetry may yet contain axes of ordinary symmetry, and the possible cases are (i) three sets of one axis each, *i.e.* three dissimilar axes, which must of necessity be at right angles to each other, (ii) one single axis, and (iii) no axis of symmetry at all. Crystals satisfying these three conditions are said to belong to the *Rhombic system*, to the *Monosymmetric* (formerly called the monoclinic) *system*, and to the *Asymmetric* (formerly called the triclinic) *system*.

Thus all crystals may be divided geometrically into the above six systems; and it is a very important fact that exactly the same division is effected by a consideration of all the physical properties, more especially the optical and mechanical ones, viz. tensional strength, the thermal and electrical properties being difficult of investigation, and also by a mathematical discussion of the possible ways of arranging a number of points in space. Crystals of the regular system behave optically like amorphous bodies, they are singly refractive and are therefore said to be *isotropic*. All other crystals are doubly refractive and are called *anisotropic*; they are divided into two classes according as they contain one direction or no direction along which a beam of light may travel and then emerge from the crystal without suffering double refraction; those possessed of this axis of single refraction are termed *optically uniaxial*. The hexagonal and quadratic crystals are both uniaxial, and optically they are undistinguishable; in both cases the tensional strength in the plane of principal symmetry varies with the direction in which it is determined, but while hexagonal crystals show three directions of minimum and of maximum strength, quadratic crystals show only two. Anisotropic crystals that are not uniaxial have been called *optically biaxial*, though they have not two directions that are truly void of the power of doubly refracting light as above defined. When a properly-cut section of a biaxial crystal is examined in 'convergent polarised light' the two optical axes are seen surrounded by dark and light rings gradually shading into each other, and as the 'interference figure' is not the same for light of any two colours, so the rings, merging more or less completely into each other, are fringed with colour, and by a careful examination of the coloured fringes it can be determined to which of the last three systems the crystal belongs; viz. if rhombic, the figure is symmetrical about both diameters A B and C D, and consequently also about the central point E; if monosymmetric, the figure is symmetrical about one or other of the diameters or about the central point, according to circumstances; if asymmetric, the figure is void of symmetry (fig. 4).

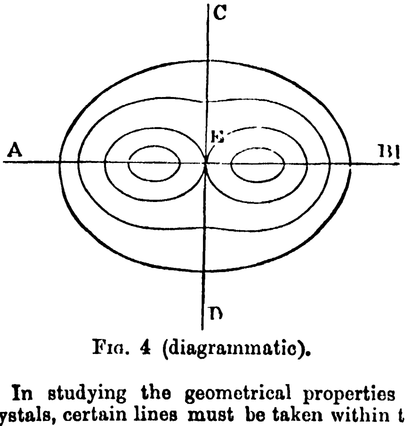


FIG. 4 (diagrammatic).

In studying the geometrical properties of crystals, certain lines must be taken within the crystal, to which all the faces may be referred; these lines, of which there must be three, are called the *crystallographical axes*, and they are represented by the letters a, b, c, while the inclinations which they make with each other are represented where necessary by the letters α, β, γ, viz. $a{:}b = \gamma$; $a{:}c = \beta$; and $b{:}c = \alpha$. In each system the crystallographic axes are chosen in such a way that the different forms may be most simply expressed. By this is to be understood that each of the different faces that together make a single crystalline form is to be related to the axes in exactly the same numerical way, or in other words the geometrical symbol for each of the faces of a form is exactly the same if the signs be omitted that denote a face to be at the top, front, right hand, &c. In the regular system the three axes of principal symmetry are chosen, and as these are all exactly similar and equal, the expression a, b, c becomes a, a, a, and as 'a' stands thus alone it may itself be considered as unity, and the axial expression thus becomes $a = a = a = 1$ or $a = 1$; the expression for the axial angles is always $\alpha = \beta = \gamma = 90°$. In the hexagonal system one set of three axes of ordinary symmetry (two of these three axes would be sufficient, but for the sake of completeness it is convenient to include the third, this is also not without its advantages), and the axis of principal symmetry, are chosen; as the first three are exactly alike, but are independent of the last, the expression for the axes a, b, c becomes a, a, a, c; one of these may be made equal to unity, most conveniently a, and the crystallographical axes are expressed $a{:}c = 1{:}c$. The axial angles are in all cases $a{:}c = 90°$ an $a{:}a = 120°$. Here notice that any and every crystal of the regular system has its axes represented by $a = b = c = 1$ and $\alpha = \beta = \gamma = 90°$, and these facts do not therefore need to be repeatedly stated, for they are comprehended in the expression 'regular system.' The same holds good with the axial angles of any and every hexagonal crystal, viz. $a{:}a{:}a = 120°$ and $a{:}c = 90°$; but with the relative lengths of the axes it is otherwise, the ratio of $a{:}c$ is not the same for any two substances, and in describing a hexagonal crystal the *crystallographical constant*, the *axial ratio* $a{:}c$, must be accurately measured and given; thus for example in lead dithionate it is as 1:1·5160, while in strontium dithionate, which has almost exactly the same form and is therefore said to be *isomorphous*, it is as 1:1·5024.

These crystallographical axes are not to be considered as definite lines, having definite lengths, but as directions, determined by the symmetry of the crystal, and consequently endowed with certain properties—*i.e.* like axes must be cut by the like number of faces at the like angles—and upon which the relative lengths of the intercepts cut off by the various faces may be calculated trigonometrically from the measurements of the interfacial angles. These angles are always measured by means of a reflecting goniometer, above the centre of whose graduated circle the edge, over which the angle is to be measured, is exactly placed by means of adjusting screws. About the same centre the crystal and a collimator or telescope may be made to revolve; the position of a beam of light incident upon the crystal, and the positions of the reflected beams from the two lustrous crystal faces, are thus measured, and the interfacial angle determined. The method of calculation may be exemplified by reference to a beryl crystal. Here there are four sets of faces, each of which, of course, cuts the axes differently, and one of these manners of cutting must be chosen as the standard (fig. 5). The basal faces (0001) cut only the vertical axis, the prismatic faces (1010) cut only the horizontal axes, and hence neither of these forms alone allows a determination of the ratio $a{:}c$.

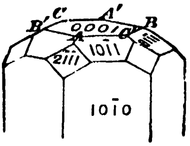


Fig. 5.

But the faces of each of the two pyramids $(10\bar{1}1)$ and $(2\bar{1}\bar{1}1)$ cut both horizontal and vertical axes; for the sake of simplicity the faces $(10\bar{1}1)$ are chosen as those of the primary pyramid, and the three horizontal axes are thus fixed as being parallel to AA′, BB′ and CC′. The angle $10\bar{1}1{:}0001$ having been measured and found

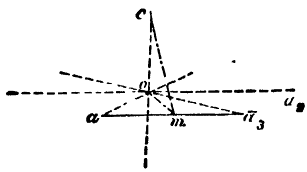


Fig. 6.

150° 3′ 20″, $a{:}c$ is easily calculated thus;

$\tan\,(180^\circ - 150^\circ\ 3'\ 20'') = \frac{oc}{om}$, but if oa = unity, then

$om = \frac{\sqrt{3}}{2}$, hence $oc = \frac{\sqrt{3}}{2}\tan\,(180^\circ - 150^\circ\ 3'\ 20'')$

$= 0{\cdot}4989$; that is, $a{:}c = 1{:}0{\cdot}4989$ (see fig. 6).

If, however, the angle of the pyramid over a terminal edge, *i.e.* $(10\bar{1}1){:}(01\bar{1}1)$ had been measured and found equal to 151° 5′ 40″, then by describing from the point a a spherical triangle cutting the face of the crystal in AB (fig. 7), the plane of principal symmetry in AC,

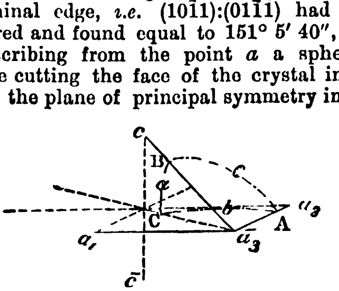


Fig. 7.

and the plane of ordinary symmetry in CB, the side a can be found from the known data, $B = \frac{1}{2}(151^\circ\ 5'\ 40'')$, $b = 60^\circ$, and $C = 90^\circ$;

$$\text{thus } \sin c = \frac{\sin b}{\sin B},\ \text{hence } c = 63^\circ\ 25'\ 20'',$$

$$\text{then } \tan\tfrac{1}{2}a = \tan\tfrac{1}{2}(c-b)\frac{\sin\frac{1}{2}(B+C)}{\sin\frac{1}{2}(C-B)}$$

$$= \frac{\tan 1^\circ\ 42'\ 40'' \times \sin 82^\circ\ 46'\ 25''}{\sin 7^\circ\ 13'\ 35''};$$

hence $\frac{1}{2}a = 13^\circ\ 15'\ 25''$, and $a = 26^\circ\ 30'\ 50''$; and lastly $\frac{\text{axis } c}{\text{axis } a}$ = tan of 26° 30′ 50″, from which the value for the vertical axis $c = 0{\cdot}4989$ is again found.

For any given crystal the axial ratios are thus exactly determinable, but where any arbitrary choice has been made, as in this instance, then the same is adopted by all subsequent observers unless good reasons are found for making an alteration.

In the quadratic system one of the two sets of two axes of ordinary symmetry, and the axis of principal symmetry, are chosen; the axial angles are in all cases 90°; the expression a, b, c, thus becomes a, a, c, and, as in the hexagonal system, the axial ratio $a{:}c$ has to be actually determined in every individual case. In the rhombic system the three axes of ordinary symmetry are chosen; the axial angles are in all cases 90°; as these three axes are not similar, the expression a, b, c, remains as such; making one equal to unity, the other two constants have to be determined in every individual case. In the monosymmetric system the axis of symmetry is chosen as one crystallographical axis; the other two axes must lie in the plane of symmetry, but otherwise their positions are perfectly arbitrary; for simplicity's sake, they are chosen parallel to two well-defined edges or faces on the crystal; in this system a, b, c, are quite independent and have to be determined, b is generally the axis of symmetry and is made equal to unity; the inclinations of $b{:}a$ and $b{:}c$ are in all cases 90°, but the inclination of $a{:}c$ (axial angle β) is variable and must be determined. In the asymmetric system the crystallographic axes are chosen quite arbitrarily; generally however they are chosen parallel to three prominent edges of the crystal; they are quite independent of each other, therefore of unequal lengths, and moreover no two of them are inclined at right angles to each other; for asymmetric crystals there are thus five constants to be determined.

Relation of faces to axes. Rationality of indices.—When a number of sets of faces on a crystal are referred to the axes whose relative lengths have been found as just explained, it is noticed that the intercepts cut off can in all cases be expressed as some simple multiple or sub-multiple of the fundamental axial lengths. This is known as the *rationality of the indices.* Thus in the case of the beryl crystal (fig. 5), while the faces of the primary pyramid cut the axes $a{:}a{:}a{:}c$ at the distances $1{:}\infty{:}1{:}0{\cdot}4989$, those of the faces $(2\bar{1}\bar{1}1)$ cut at $1{:}2{:}2{:}0{\cdot}9978$; here 1 is 1×1, 2 is 2×1, and $0{\cdot}9978$ is $2 \times 0{\cdot}4989$, and the numbers 1, 2, 2, 2 are here indices. The indices are generally expressed by very simple numbers, as 1, 2, 3, 4, 5, 6, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{2}{3}$, &c., but in some cases the ratios are not so simple.

The indices of a face may be measured in two ways—the one known as Neumann's system, and the other as Miller's. Let the relative lengths of any set of primary axes be expressed by the letters a, b, c, and let there be another face on the crystal which cuts the axes at some other distances, say $2a$, $3b$, $4c$, from their centre. According to Neumann the indices of this face are $\frac{2a}{a}$, $\frac{3b}{b}$, $\frac{4c}{c}$ *i.e.* 2, 3, 4; following Miller, however, the indices are the reciprocals of those of Neumann, viz. $\frac{a}{2a}$, $\frac{b}{3b}$, $\frac{c}{4c}$, *i.e.* $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, or, simplifying, the expression becomes 6, 4, 3.

Of course there will be more than one face having this symbol, the number depending on the symmetry of the crystal, but the relative positions of any of these may be exactly denoted by the following device. In all the systems the extremities of the axes forming the front upper right corner are called positive, and are simply written *a*, *b*, *c*, &c., while the opposite extremities are called negative, and are written $\bar{a}$, $\bar{b}$, $\bar{c}$, &c. Thus taking the pyramid of the beryl crystal, and using Miller's symbols, we have the axes and faces numbered as in figs. 8 and 9.

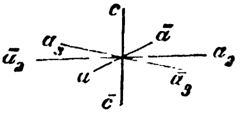


FIG. 8.

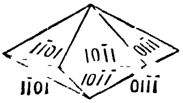


FIG. 9.

The axial ratios once determined, it is possible from them and the symmetry to say at once what forms are possible, and to calculate their interfacial angles, &c.; but what forms will actually occur, under any conditions, cannot be predicted; their existence depends on external conditions, as presence of impurities in the solution, nature of the solvent, temperature, and speed of growth. Mineralogists and crystallographers often pay too much attention to the finding of new or numerous forms upon specimens without attempting to determine what were the conditions necessary for the production of these forms, which is the only point of real interest.

The following may serve as an example of the way in which the symmetry of a crystal determines the number and position of the faces of a form. In fig. 10 the three similar crystallographic axes of the beryl crystal (fig. 5) are represented by the lines a_1, a_2, and a_3, while the principal axis *c* is perpendicular to the plane of the paper. Suppose a face of the hexagonal pyramid to be present in the front, upper, middle segment, *i.e.* $10\bar{1}1$, then this demands the existence of a face $1\bar{1}01$, because the plane passing through axis a_1 and the vertical axis *c* is a plane of symmetry; the presence of $1\bar{1}01$ demands the existence of $0\bar{1}11$, because the plane containing a_2 and *c* is a plane of symmetry; further, these three faces demand the existence of other three, viz. 0111, $\bar{1}101$, $\bar{1}011$, because the plane a_3c is a plane of symmetry; and lastly, these six planes demand the presence of other six on the under part of the crystal, viz. $10\bar{1}\bar{1}$, 0111, 1101, $\bar{1}01\bar{1}$, $01\bar{1}\bar{1}$, 1101, because the plane containing axes a_1, a_2, a_3 is a plane of symmetry. And with these twelve faces the form is complete, for the other three planes of symmetry belonging to this system are already satisfied.

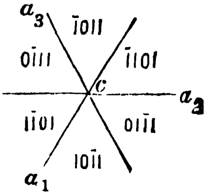


FIG. 10.

It would be very tedious and redundant to denote this or any other form by writing the symbols of all its faces, and it is therefore customary to write the symbols of only one, generally one in the front, upper, right corner, and to inclose it in brackets thus $(10\bar{1}1)$ for the pyramid in question. The general shape of a form is not essentially altered by varying the indices within certain limits; thus $(30\bar{3}1)$ and $(10\bar{1}3)$ (figs. 11 and 12) as well as $(10\bar{1}1)$ (fig. 9), represent hexagonal pyramids, though the form $(30\bar{3}1)$ is very high and pointed, while the form $(10\bar{1}3)$ is proportionally low and flat-looking. These may all be expressed by one general symbol $(m0\bar{m}1)$ (where *m* has any value *between* 0 and ∞), and are said to be particular forms of one general form $(m0\bar{m}1)$; thus fig. 12 represents the particular form for a crystal of beryl when $m = \frac{1}{3}$, for $10\bar{1}3$ is the same as $\frac{1}{3}0\bar{\frac{1}{3}}1$, *i.e.* $m0\bar{m}1$.

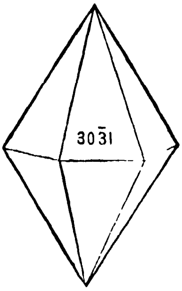


FIG. 11.

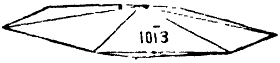


FIG. 12.

But if the index *m* has the value of 0, then the six upper faces of the pyramid fall together into one plane, and so also do the six lower faces, so that the form (0001) consists only of two faces parallel to each other and also to the plane of principal symmetry; if *m* has the value of ∞, then each of the upper six faces becomes coincident with the subjacent bottom face, and the form $(\infty 0\bar{\infty}1)$, or, as it is more usually written, $(10\bar{1}0)$, consists of six faces, all parallel to the axis of principal symmetry, and consequently not limited towards either end; these two forms (0001) the basal plane, and $(10\bar{1}0)$ the prism, may be called open forms, and can never occur alone on a crystal. They contain no variable quantity, and may therefore be called *fixed forms*, while the pyramid is a *variable form*.

These two forms, the basal plane and the prism, though derivable from the pyramid and related to it in position, are obviously quite distinct forms, and all are so far independent of each other that any one may or may not occur on a crystal in conjunction with the others. By varying the indices in every possible manner, as just indicated, it is easy to determine the shapes and number of all such fundamental or general forms for every system; and indeed it is only possible to grasp the relationships existing between them by regarding them as being derived from one perfectly general form ($mn1$). The number of individual forms is very limited; the following is a complete list of their symbols and names.

Regular system.—($mn1$), ($mm1$), ($mn0$), ($mm0$), (111), (001), (110), called respectively *hexakis octahedron, triakis octahedron, tetrakis hexahedron, trapezohedron, octahedron, cube* or *hexahedron*, and *dodekahedron*; the last three are fixed forms.

Hexagonal system.—($m\bar{p}\bar{n}1$), (*Note*: in the symbols for all hexagonal forms $m+n+p=0$). ($m\bar{p}\bar{n}0$), in both these cases the ratio $\frac{m}{n}$ varies only between 1 and 2; ($m0\bar{m}1$), (1010), ($2m\bar{m}\bar{m}1$), ($2\bar{1}\bar{1}0$), and (0001), called respectively the *dihexagonal pyramid* and *prism*, the *hexagonal pyramids* and *prisms of the first order*, and *of the second order*, and the *basal plane*.

Quadratic system.—($mn1$) and ($mn0$), where the ratio $\frac{m}{n}$ varies *between* 1 and ∞; ($mm1$), ($mm0$), ($m01$), ($m00$), and 001; the forms are called the *diquadratic pyramid* and *prism*, the *quadratic pyramid* and *prisms of the first order*, and *of the second order*, and the *basal plane*.

Rhombic system.—($mn1$), ($mn0$), (001), called respectively *pyramids prisms* or *domes*, and *basal plane* or *pinacoids*.

Monoclinic system.—The same forms exist as in the rhombic system, but here, owing to low order of symmetry, all the pyramids and some of the domes are composed of independent halves, which are distinguished as + or −, or by more fully denoting the position of the face; thus ($mn1$) and ($mn\bar{1}$).

Asymmetric system.—The same forms exist as in the rhombic system, but here, owing to the lack of symmetry, all the pyramids are composed of independent quarters, thus ($mn1$), ($m\bar{n}1$), ($mn1$), and ($m\bar{n}\bar{1}$), and all the prisms and domes are composed of independent halves, thus ($mn0$) and ($m\bar{n}0$).

The forms just described are collectively called *holohedral* or whole or complete-faced forms, to distinguish them from other forms known as *hemihedral* or half-faced, and *tetartohedral* or quarter-faced.

Hemihedral forms may be considered as derived from the holohedral forms by resolving these by a set or sets of planes of symmetry into a number of equal segments, when the faces contained in any one segment belong to the one hemihedral form, while those contained in the adjacent segment or segments belong to the other hemihedral form, and so on all round the crystal.

The hemihedral forms of the hexagonal system being very important will be taken by way of example. Any holohedral hexagonal form may be divided into segments in three different ways:—

Firstly, by the plane of principal symmetry and one of the two sets of three planes of ordinary symmetry; making then the adjacent faces independent, the *rhombohedral hemihedral* forms are produced. Numbering the faces of the most general form, the dihexagonal prism, as in fig. 13 it is seen that the faces are divided thus:

1 2 3 4 5 6 7 8 9 10 11 12
1 2 3 4 5 6 7 8 9 10 11 12

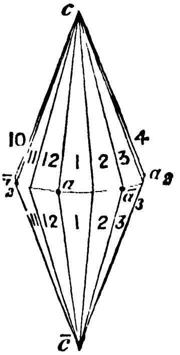


FIG. 13.

The two forms

1 2 . . 5 6 . . 9 10 . .
. . 3 4 . . 7 8 . . 11 12

and

. . 3 4 . . 7 8 . . 11 12
1 2 . . 5 6 . . 9 10 . .

are known as the + and − *scalenohedrons* (figs. 14 and 15), which differ from each other in position and in physical properties. Just as in the holohedral division, so here, the indices of only one face is written within brackets to denote the whole form, but to distinguish it from the symbol of the original pyramid the prefix κ is added; thus the symbols for the two scalenohedrons are $\kappa(m\bar{p}\bar{n}1)$ and $\kappa(pn\bar{m}1)$. By varying the values of these indices m, n, p in every possible way, or by dividing all the other holohedral forms into segments in the same fashion, it is found that there are produced two other new forms, the + and − *rhombohedrons* $\kappa(m0\bar{m}1)$ and $\kappa(0m\bar{m}1)$, figs. 16 and 17; while the following forms already mentioned in the holohedral division appear again without apparent alteration, viz. ($m\bar{p}\bar{n}0$), ($10\bar{1}0$), ($2m\bar{m}\bar{m}1$), ($2\bar{1}\bar{1}0$), and (0001). But the con-

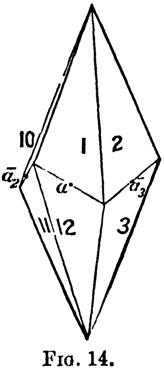


FIG. 14.

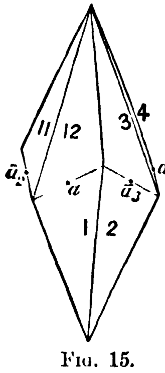


FIG. 15.

stancy of these latter forms in both divisions is not real, as the physical properties are different; this is especially to be seen in the manner in which they yield to the action of solvents, whereby little pittings or *etch-figures* are produced which vary in their symmetry according as the forms are holohedral or hemihedral. It

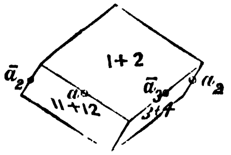


Fig. 16.

is to be understood that practically the holohedral and hemihedral forms are perfectly distinct, that is, a given substance shows the forms of only one of the two classes, never those of the other. For example, calcite frequently occurs in the form of the scalenohedron (3$\bar{1}\bar{2}$1), fig. 14, and is therefore obviously hemimorphous, but it also frequently occurs in the form of fig. 18, and

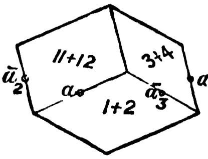


Fig. 17.

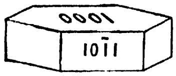


Fig. 18.

this may be either a holohedral or a hemihedral crystal, but the fact that such crystals cleave with the utmost readiness parallel to the faces of the positive rhombohedron κ(*m*0*m̄*1) at once removes it from the class of holohedral crystals; its hemimorphous nature is also proved by other physical properties.

A holohedral hexagonal form may be divided into segments, *secondly*, by means of the two sets of three planes of ordinary symmetry, whereby the *pyramidal hemihedral forms* are produced; for example:—

~~1~~ 2 ~~3~~ 4 ~~5~~ 6 ~~7~~ 8 ~~9~~ 10 ~~11~~ 12
~~1~~ 2 ~~3~~ 4 ~~5~~ 6 ~~7~~ 8 ~~9~~ 10 ~~11~~ 12

The uncrossed faces π(*pnm̄*1) are represented on a crystal of apatite by figure 19 where π(*pnm̄*1) = π(21$\bar{3}$1). All other forms are exter-

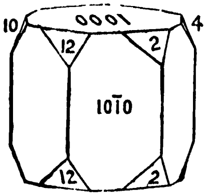


Fig. 19.

nally the same as in the holohedral division, with the exception of π(*pnm̄*0). These two new forms are called the pyramid and prism of the third order.

Thirdly, by means of the two sets of three planes of ordinary symmetry and the plane of principal symmetry, whereby the *trapezohedral hemihedral* forms are produced; for example:—

~~1~~ 2 ~~3~~ 4 ~~5~~ 6 ~~7~~ 8 ~~9~~ 10 ~~11~~ 12
1 ~~2~~ 3 ~~4~~ 5 ~~6~~ 7 ~~8~~ 9 ~~10~~ 11 ~~12~~.

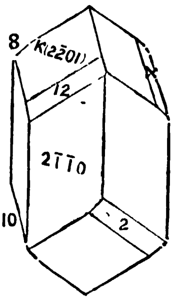
These forms are distinguished by the prefix τ, the crossed faces being τ(*mp̄n̄*1); such forms have not been actually observed.

The *tetartohedral forms* before referred to may be considered as being produced by the superposition of two different hemihedræ upon the same crystal. As there are in the hexagonal system three classes of hemihedrie, there can be obtained two or perhaps three different classes of tetartohedrie. In the following schemes the faces suppressed by the rhombohedral, pyramidal, and trapezohedral, hemihedræ are respectively crossed /, —, or \.

First, the *rhombohedral tetartohedrie* is produced thus:—

$$\begin{array}{cccccccccccc} \cancel{1} & \cancel{2} & \sout{3} & 4 & \cancel{5} & \cancel{6} & \sout{7} & 8 & \cancel{9} & \cancel{10} & \sout{11} & 12 \\ \sout{1} & 2 & \cancel{3} & \cancel{4} & \sout{5} & 6 & \cancel{7} & \cancel{8} & \sout{9} & 10 & \cancel{\sout{11}} & \cancel{12} \end{array}$$

The faces of a dihexagonal pyramid remaining uncrossed, viz. $_2{}^4{}_6{}^8{}_{10}{}^{12}$, form a rhombohedron of the third order, written κπ(*mn̄p̄*1), which is exhibited in fig. 20 of a copper silicate (diaspore) crystal, where the indices are κπ(14.$\bar{1}\bar{3}$.$\bar{1}$.6).



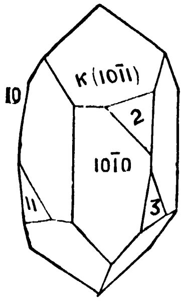


Fig. 20. Fig. 21.

Secondly, the *trapezohedral tetartohedrie* is produced thus:—

$$\begin{array}{cccccccccccc} \bcancel{1} & 2 & \xcancel{3} & \cancel{4} & \bcancel{5} & 6 & \xcancel{7} & \cancel{8} & \bcancel{9} & 10 & \xcancel{11} & \cancel{12} \\ \cancel{1} & \xcancel{2} & 3 & \bcancel{4} & \cancel{5} & \xcancel{6} & 7 & \bcancel{8} & \cancel{9} & \xcancel{10} & 11 & \bcancel{12}, \end{array}$$

the form κτ(*npm̄*1) consisting of the six uncrossed faces $^2{}_3{}^6{}_7{}^{10}{}_{11}$ being known as the trigonal trapezohedron, and in the figure representing a quartz crystal the faces of such a form, viz. κτ(51$\bar{6}$1) are shown (fig. 21).

Thirdly, the scheme

$$\begin{array}{cccccccccccc} \bcancel{\sout{1}} & 2 & \bcancel{\sout{3}} & 4 & \bcancel{\sout{5}} & 6 & \bcancel{\sout{7}} & 8 & \bcancel{\sout{9}} & 10 & \bcancel{\sout{11}} & 12 \\ \sout{1} & \bcancel{2} & \sout{3} & \bcancel{4} & \sout{5} & \bcancel{6} & \sout{7} & \bcancel{8} & \sout{9} & \bcancel{10} & \sout{11} & \bcancel{12} \end{array}$$

shows a form bounded by six faces meeting the vertical axis above, but no face meeting it below. It is doubtful whether this tetartohedrie has been observed; for exactly the same form would be produced by making either of the forms π(*mp̄n̄*1) or τ(*mp̄n̄*1) hemimorphous or half-sided.

Hemimorphism may be described as the dividing of the faces of a crystalline form into two independent halves, the one half cutting the one extremity of an axis of symmetry, and the other half the other extremity of the same axis. Hemimorphism is to be found in the first five systems in holohedral, hemihedral, and tetartohedral, divisions alike; it is supposed to be due to asymmetry of the atoms in the molecule, and the solutions of the substances showing this phenomenon, as tartaric acid, milk, sugar, &c., are generally optically active. It is to be noticed that some divisions of crystals are necessarily hemimorphous. Thus the hexagonal trapezohedral tetartohedral forms are hemimorphous to the axes of ordinary symmetry.

The hexagonal crystals are thus divided into the following six or seven distinct classes: (*a*) holohedral; (*b*) hemihedral, and that of three kinds, rhombohedral, pyramidal, and trapezohedral; and (*c*) tetartohedral, and that of at least two kinds, rhombohedral and trapezohedral, and possibly another; and lastly to each of these six classes there may or may not be assimilated also hemimorphism, making in all twelve or possibly thirteen divisions of hexagonal crystals, in only one of which can any substance ever crystallise.

These six or seven classes are to be considered as being due to the different arrangements of the molecules in the crystal, but among these different molecular arrangements there are certain regularities common which group them all together into one general system. It is to be noted that all hemihedral and tetartohedral divisions are invariably possessed of fewer planes of symmetry or of planes of a lower degree of symmetry than are the holohedral forms; thus the trapezohedral hemihedral forms and all tetartohedral forms of the hexagonal system are possessed of no plane of symmetry whatever, *i.e.* as defined at the commencement of this article; but such forms do not, therefore, belong to the asymmetric system, for in the first place they show a perfect regularity in the recurrence of equal faces and angles in sets of three or of six, which an asymmetric crystal can never do, and secondly they show none of the physical properties of these crystals, but properties that are either identical with those of the hexagonal holohedral crystals, or are in the main of the same kind, differing only just so much as might be expected from the lower degree of symmetry they possess.

Just as hexagonal crystals are divided into a number of distinct classes, so also are the crystals of the other systems as far as their varying symmetry allows. Thus regular crystals are either (*a*) holohedral, (*b*) hemihedral, and that of three kinds, viz. tetrahedral, pentagonal, or plagihedral, or (*c*) tetartohedral of one kind only; the quadratic crystals are subdivided exactly like the hexagonal ones; the rhombic crystals are either (*a*) holohedral or (*b*) hemihedral; and the monosymmetric and asymmetric crystals can show neither hemihedrie nor tetartohedrie.

There still remains another regularity met with in the forms of crystals, viz. the symmetrical growth of two or more crystals as one individual. Such a complex is called a *twin* or *trilling*, and in such the component individuals are definitely related as regards position, viz. the one crystal generally occupies such a position that were it rotated through 180° about a particular line, called the *twin axis*, all its faces &c. would then be exactly parallel to those of other crystals. The plane at right angles to the twin axis is called the *twin plane*, and in many instances the two individuals meet in this plane, and it is then also termed the *contact plane*; but in other instances the two individuals penetrate each other in a perfectly irregular manner, and there is then no definite contact-plane. The formation of a twin crystal is probably explained by extreme viscosity of the solvent, or of an insufficient lapse of time between the separation of two molecules from a solution and their approximation to form a single solid particle, and for either of which reasons the molecules would not be able to become exactly parallel, which must be the most stable position, but would take up the next most stable position by reason of the molecule being originally more nearly in that position. As a plane of symmetry for the external form is also a plane of symmetry of the intermolecular force, which varies with the direction in which it is exercised, so a plane of symmetry can never be a twin plane, else the two individuals would be exactly parallel; that is, they would be identical: further, as the arrangement of the molecules, and consequently the external form, depends on this same intermolecular force, so the twin plane and axis are invariably connected with the external form; generally the twin plane is a possible crystalline face, and often one that is expressed by a very simple symbol. Twin or complex crystals are often characterised by re-entering angles, but these are frequently either so small as to be unnoticeable or are not present, and the crystal then affects a symmetry that it does not really possess.

The following figs. represent rhombic aragonite crystals; fig. 22, a simple crystal, and fig. 23, a twin, showing re-entering angles, the twin plane being the prism face; and lastly, fig. 24 represents a trilling, showing only the forms (110) and (001), which externally appears very like a hexagonal crystal, except that two of the vertical faces are a little nicked because the angle of the prism (110) is not exactly 120°. The real nature of such compound crystals is most easily detected by their optical properties, a section cut parallel to the base at once resolving itself in a parallel beam of polarised light into a number of segments distinguished from each other by difference of colour or luminosity, and whose relative positions can readily be determined by optical examination.

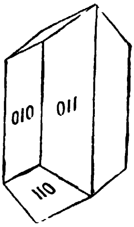


FIG. 22.

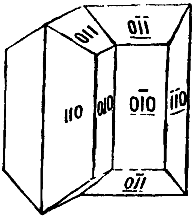


FIG. 23.

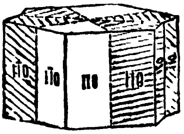
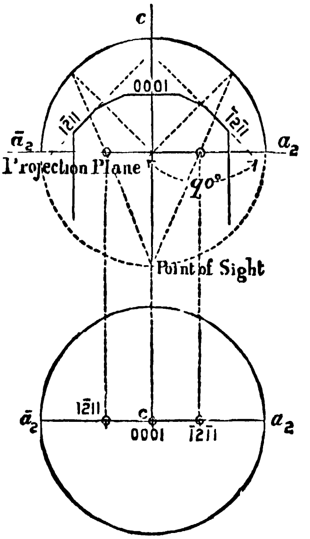


FIG. 24.

Besides representing the form of crystals by parallel projections, as in the various figures, these forms are often also represented in a totally different manner, viz. by spherical projection. From a central point within a crystal, imagine a sphere of any radius described, and from its centre a line let fall perpendicularly on to every crystalline face and produced until it cuts the surface of the sphere. The positions of the faces are thus recorded by as many points upon the surface of the sphere, and their positions may very conveniently be represented upon a flat surface by making a diametral section of the sphere bringing the recording plane and one extremity of the diameter at right angles to that plane into the point of view, whereby great labour in drawing and calculating is saved, as all great circles on the sphere appear in the projection as straight lines or as arcs of circles. In the regular, hexagonal, and quadratic, systems the diametral section is always drawn parallel to the plane of principal symmetry, in the rhombic system to the basal plane, in the monosymmetric and asymmetric systems it is drawn perpendicular to the faces of the prisms. Thus the beryl crystal, fig. 5, as far as the sphere lies in the plane of this paper, appears as in fig. 25, and the position of the three faces, when drawn upon the plane of principal symmetry, as in fig. 26; the one straight line joining the three points shows that they are in the same zone, that is, are all parallel to one common direction, and therefore their intersecting edges are parallel, and this fact is very easily noticed or tested when the crystal is mounted on the goniometer for measuring. The completed projection appears as in fig. 27, where zones are all indicated by the various lines circular or straight. This method of projection also allows of the positions of optical axes, cleavage planes, &c., being shown.



Figs. 25 and 26.

It now only remains to mention a few points concerning the growth and actual appearance of the faces of a crystal, beyond those mentioned on p. 278. A crystal once formed in a solution and continuing to increase in size, every face, or at least every face of any set of faces, would receive a deposit of the same thickness, and an ideally perfect crystal as represented in the figures would result, were it not that the liquid in depositing the solid substance altered its specific gravity, and currents being thus generated different parts of the crystal are thus subjected to different conditions, and the several faces receive unequal deposits of new material. In consequence, the intersections of the similar faces and their superficial extent are often very dissimilar, though every face always remains exactly parallel to its original position, and the interfacial angles are constant. This so-called *distortion* is often brought about or increased by the crystal becoming attached by an end or side to other crystals, or to the containing vessel. Thus fig. 28 represents an alum crystal that has lain on the flat bottom of the containing vessel, and fig. 29 represents the ideal form such as may be obtained by constantly changing the position of the growing crystal.

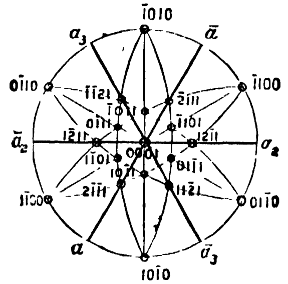


Fig. 27.

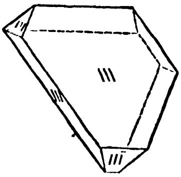


Fig. 28.

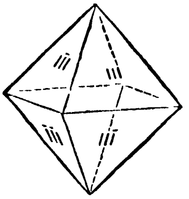


Fig. 29.

When new material is very quickly presented to a growing crystal, it is often noticed that the acuter solid angles grow extremely rapidly, shooting out into long needle-like points, and often other acicular points will start from along the first, and thus fern-like forms are produced; all such growths are termed *crystalline skeletons*; when the rate of deposit becomes less the needles almost cease to grow in the direction of their length, but increase continually in breadth and thickness until they touch each other, and the crystal returns to its original appearance, though almost invariably it will contain a great number of larger or smaller cavities, filled with the mother-liquor, and, as already mentioned, these cavities exhibit an arrangement or a form that corresponds with the general symmetry of the crystal. Some substances, as ammonium chloride, metallic silver, &c., are very prone to form such *dendritic forms*, while with other substances, as platinum-potassium chloride, if existing crystals were not able to take up the new material, a multitude of minute crystals would at once form. The direction of these skeleton arms is always coincident with some crystallographic direction, and they are in reality made up of numerous crystals, in exactly parallel position. It has been mentioned that the faces of crystals are often striated; the striæ consist of numerous alternating faces of one or more forms; thus nitre crystals are vertically striated on the prism and pinacoid faces by reason of these faces being repeated alternately very many times.

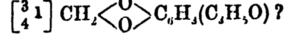
Finally it may be useful briefly to describe such a microscope as is used for the examination of minute or growing crystals, or for the examination of rock sections. In this connexion reference should be made to the papers of Behrens (*Royal Micros. Soc. Journ.*, 1882) and others, on the microchemical reactions by which minute fragments of minerals &c. may be analysed qualitatively by converting their constituents into crystalline precipitates that may be recognised under the microscope. The essential parts of the microscope are the same as in every other instrument, the parts specially concerned in crystallographic work being the following. The stage can be rotated freely about the optical centre of the instrument, and is brought exactly into that position by a couple of adjusting screws; the circumference is graduated into degrees, and fractions can be read by a vernier. The eye-pieces contain crossed (rectangular) threads, and these always occupy a fixed position by reason of a pin in the eye-piece and a notch in the outer tube. Plane angles of crystals that lie suitably, the angles between the lines of inclosures &c., are easily measured by the rotating stage and the cross of the eye-piece. The fine adjustment-screw for focussing is of known pitch, and is provided with a head divided on its circumference. By using a high power and a rather thick specimen it is easy to determine the refractive index not only of solids but of liquids (Sorby). In the eye-piece can be fitted a micrometer scale, and by using this and the micrometer screw the interfacial angles of minute crystals can be measured, though the method is one that would only be used if the goniometric measurement were not possible. During the cutting or grinding of sections, especially rock sections, the crystals often cleave, and the positions of the planes of cleavage are at once determined from the fine parallel hair-like cracks in the specimen. Underneath the stage a polarising prism is quickly put into position so that its polarising plane is parallel to one of the cross threads in the eye-piece; crystals may then be examined for dichroism. Above the stage, and most conveniently over the eye-piece, a second polarising prism may be placed or rapidly removed; it may be rotated about the central axis, and the amount of rotation is approximately shown on a small divided circle. When the two prisms are crossed, isotropic and anisotropic crystals are at once distinguished, unless the crystalline plate is at right angles to the optical axis, but in this case the interference figure can be obtained as described below; further, if the crystal be anisotropic, twinning is generally at once recognised, and, with the help of the rotating stage, the relationships of the different parts are determined, by comparing the depolarising directions among themselves and with the edges of the crystal; similarly in a simple anisotropic crystal the angles between the depolarising directions and the edges may be measured, and the system of crystallisation thus determined when the examination of the external form alone would not have been conclusive; and even when the external form has been destroyed, or when it has been lost by reason of the crystal growing until it filled the whole space that happened to be at its disposal, the examination of the cleavage cracks, lines of inclosures, and depolarising directions, is often sufficient to determine the crystalline system. The relationship between depolarising directions and edges may be used for discriminating between different substances crystallising in the monosymmetric or asymmetric systems, as the various felspars. Finally anisotropic crystals lying in suitable positions can be examined for their interference figures by removing the eye-piece, but retaining both polarising prisms, placing a small, very short, focus-lens above the lower prism and directly below, but quite close to, the crystal, and lastly using a short focus objective and bringing it down rather close to the specimen. The interference figures thus observed are certainly very small, and an extra lens is sometimes inserted above the objective to magnify them, but the angle of view is thereby diminished. Uniaxial and biaxial crystals are thus at once distinguished, and if the former show any marked amount of circular polarisation, or the latter any marked amount of dispersion for the various colours, these phenomena can also be noticed, especially if use is made of red and blue glasses to simplify the phenomena; such glasses are also used in the measurement of the angles between depolarising directions and crystalline edges. H. B.

CUBEBS.—The fruit of *Piper Cubeba*, a native of Java. It contains a volatile oil (from which 'camphor of cubebs' may be separated), a crystalline substance cubebin, an acid resin cubebic acid, and an indifferent resin (Monheim, *J. chim. Méd.* 11, 352; Blanchet a. Sell, *A.* 6, 294; Müller, *A.* 2, 90; Winckler, *A.* 8, 203; Soubeiran a. Capitaine, *A.* 31, 190; 34, 311; *J. Ph.* 26, 75; Aubergier, *Rev. Scient.* 4, 220; Schmidt, *Ar. Ph.* [2] 191, 1; Schaer a. Wyss, *Ar. Ph.* [3] 6, 316; Oglialoro, *G.* 5, 467).

Oil of Cubebs. Contains dipentinene, the hydrochloride of which $C_{10}H_{16}2HCl$ melts at 49°, but consists chiefly of hydrocarbons boiling between 250° and 270°, amongst which is a sesquiterpene $C_{15}H_{24}$ (275°). V.D. 6·73 (calc. 7·05), whose hydrochloride $C_{15}H_{24}2HCl$ melts at [118°] (Wallach, *A.* 238, 80) or [131°] (S. a. C.).

Camphor of Cubebs $C_{15}H_{26}O$. [67°]. (148°). Occurs only in old cubebs. Trimetric crystals (from alcohol-ether). Lævorotatory. At 230° it is split up into water and cubebene $C_{15}H_{24}$ (Schmidt, *B.* 10, 189; *cf.* Berthelot, *Bl.* [2] 11, 3).

Cubebin $C_{10}H_{10}O_3$

i.e. 
$\left[\begin{smallmatrix}3 & 1\\ 4 & \end{smallmatrix}\right] CH_2{<}\substack{O\\ O}{>}C_6H_3(C_3H_5O)$? [125°]. S. (alcohol) 1·31 at 12°. S. (ether) 3·75. Extracted by alcohol from cubebs after removal of the

essential oil by steam distillation (Schuck, *N. Repert. Pharm.* 1, 213; Steer, *A.* 36, 331; Weidel, *Sitz. W.* 74 [2] 377; Schär, *Ar. Ph.* [3] 25, 531).

Properties.- Small needles (from alcohol); v. sl. sol. water. Conc. H_2SO_4 colours it crimson. HCl and HI have no action on it.

Reactions.—1. $KMnO_4$ on warming oxidises it to oxalic acid and a resin, from which, after extracting with $CHCl_3$, a crystalline residue of piperonylic acid $C_8H_6O_4$ [228°] is obtained.—2. When heated with *acetic anhydride* and *sodium acetate* to 140° C. it yields $C_{20}H_{18}O_5$ [78°], which can be obtained pure by crystallisation from alcohol (Pomeranz, *M.* 8, 466).—3. *Potash-fusion* gives CO_2, HOAc, and protocatechuic acid.—4. HNO_3 gives oxalic and picric acids.—5. *Nitrous acid* gives yellow crystals of nitrocubebin $C_{10}H_9(NO_2)O_3$, which dissolves in aqueous KOH, forming a violet solution.—6. Br, added to a solution of cubebin in chloroform, gives $C_{10}H_7Br_3O_2$, which separates from boiling xylene in white crystals.

Benzoyl derivative $C_{10}H_9BzO_3$. [147°] (Pomeranz, *M.* 9, 323).

Cubebic acid $C_{11}H_{16}O_4$ (Schulze, *Ar. Ph.* [3] 2, 388); $C_{13}H_{14}O_7$ (Schmidt, *Ar. Ph.* [2] 191, 1). A resinous acid extracted from cubebs by ether, freed from volatile oil by steam-distillation, and purified by re-crystallisation of its Ba salt (Bernazik, *C. C.* 1864, 191). Amorphous, insol. water and acids, v. sol. alcohol, ether, and alkalis.

CUDBEAR. A name given to a variety of archil, being also prepared from lichens, chiefly of the genus *Lecanora*.

CUMALIC ACID *v.* Coumalic acid.

CUMARHYDRIN *v.* Coto bark.

ψ-CUMENE $C_6H_3(CH_3)_3$ [1:3:4]. *i-Tri-methyl-benzene.* Mol. w. 120. (169½° i.V.) (Jacobsen, *B.* 19, 2513). S.G. $^{\underline{0}}$ ·8043; $^{\underline{20}}$ ·8530. H.F.p. 1310. H.F.v. –1590 (*Th.*). *Dielectric constant* 2·431 at 14° (Negreano, *C. R.* 104, 423). μ_D 1·481. Occurs in all kinds of petroleum (American, Russian, &c.) (Engler, *B.* 18, 2234; *cf.* Mansfield, *C. J.* 1, 241; *A.* 69, 179; Ritthausen, *J. pr.* 61, 79; Beilstein a. Kögler, *A.* 137, 317).

Formation.—1. From bromo-*m*-xylene and bromo-*p*-xylene by treatment with MeI and sodium (Fittig, *A.* 139, 187; 151, 257, 286).—2. From di-bromo-toluene, MeI, and sodium (Jannasch, *A.* 176, 286).—3. From phorone (derived from acetone) by treatment with P_2O_5 (Jacobsen, *B.* 10, 855).—4. From toluene, MeCl, and Al_2Cl_6 (Friedel a. Crafts, *A. Ch.* [6] 1, 461). 5. By boiling pseudo-cumyl-hydrazine with aqueous $CuSO_4$ (Haller, *B.* 18, 92).

Preparation. - The mixture of ψ-cumene and mesitylene obtained by the distillation of coal tar is sulphonated by agitation with cold conc. H_2SO_4; on adding water a portion of the ψ-cumene sulphonic acid is ppd., the remaining acids are converted successively into their Ba salts, chlorides, and amides, and the latter are separated by crystallisation from alcohol, in which the amide of ψ-cumene sulphonic acid is sparingly soluble. The sulphamide is then converted into ψ-cumene by heating with fuming aqueous HCl at 175° (Jacobsen, *B.* 9, 256). The sulphonic acids of ψ-cumene and mesitylene may also be separated by heating with HClAq at 100° for one hour, when the latter only undergoes hydrolysis (Armstrong, *B.* 11, 1697). ψ-Cumene sulphonic acid is decomposed by distillation with dilute H_2SO_4 in a current of steam, hydrolysis beginning at 115° (Armstrong a. Miller, *C. J.* 45, 148).

Reactions.—1. Readily attacked by halogens. In the *dark* 1 mol. of bromine produces mono-(eso)-bromo-pseudo-cumene $C_6H_2Me_3Br$ [73°]; further bromination yields di- and tri-(eso)-bromo-pseudo-cumene (C_6HMe_3Br and $C_6Me_3Br_3$) of melting-points [61°] and [226°] respectively. Direct *sunshine* acts like *heat*, causing the substitution to take place in the CH_3 groups; 1 mol. Br produces a liquid ω-bromo-(pseudo)-cumene (pseudo-cumyl bromide) $C_6H_3(CH_3)_2.CH_2Br$; 2 mols. bromine produce ω_1-ω_2-di-bromo-pseudo-cumene $C_6H_3(CH_3)(CH_2Br)_2$ which melts at 97° (Schramm, *B.* 19, 216).—2. Converted by boiling with Al_2Cl_6 into toluene, *m*-xylene, a little *p*-xylene, mesitylene, durene, and isodurene (Anschutz, *A.* 235, 186).—3. *Methylene chloride* and Al_2Cl_6 give durene, tetra-methyl-anthracene [c. 163°], hexa-methyl-anthracene [c. 220°] and $C_{18}H_{18}$ [c. 290°] (Friedel a. Crafts, *A. Ch.* [6] 11, 263).—4. Gives a tri-nitro- derivative [185°].—5. Dilute HNO_3 gives two di-methyl-benzoic acids and a little $C_6H_3Me(CO_2H)_2$.

ψ-Cumene hexahydride C_9H_{18}. (137°). S.G. $\frac{0}{0}$ ·7812; $\frac{20}{0}$ ·7667. From ψ-cumene, HI, and P. HNO_3 gives tri-nitro-ψ-cumene. Br and Al_2Br_6 give tri-bromo-ψ-cumene (Konovaloff, *C.C.* 1887, 1133). Probably identical with nonaphthene.

Cumene C_9H_{12} *i.e.* C_6H_5Pr. *Isopropyl-benzene.* Mol. w. 120. (153° i.V.). S.G. $^{\underline{0}}$ ·8776; $^{\underline{25}}$ ·8577 (Silva, *Bl.* [2] 43, 317); $^{\underline{0}}$ ·8798; $^{\underline{25}}$ ·8587 (Paternò a. Pisati, *G.* 3, 574).

Formation.—1. By distilling cuminic acid with baryta or lime (Gerhardt a. Cahours, *A. Ch.* [3] 1, 87, 372; 14, 107; *A.* 38, 88; *cf. A.* 220, 27).—2. From isopropyl bromide, benzene, and Al_2Br_6 (Gustavson, *B.* 11, 1251; R. Meyer, *J. pr.* [2] 34, 98). In the same way from *n*-propyl bromide, inasmuch as *n*-propyl bromide is converted by heating with Al_2Br_6 into isopropyl-bromide (Kekulé a. Schrötter, *B.* 12, 2280).—3. By acting with isopropyl chloride or *n*-propyl chloride on benzene in presence of aluminium chloride (Silva; Claus a. Schulte, *B.* 19, 3012).—4. As a by-product by the action of allyl chloride on benzene in presence of Al_2Cl_6.—5. By the action of di-chloro-acetone in presence of Al_2Cl_6 on benzene as a by-product (Silva).—6. From benzylidene chloride and $ZnMe_2$ (Liebmann, *B.* 13, 45).—7. From iso-propyl iodide, bromo-benzene, and sodium (Jacobsen, *B.* 8, 1260).

Reactions.—1. *Chromic mixture* gives benzoic acid.—2. Br and Al_2Br_6 give C_6Br_6, isopropyl bromide, and tri-bromo-propane (c. 218°).

Cumene tetrahydride C_9H_{16}. (155°). Occurs in small quantity in oil of resin (Renard, *A. Ch.* [6] 1, 239).

Cumene hexahydride C_9H_{18}. (c. 149°). S.G. $^{\underline{20}}$ ·787. Occurs in oil of resin (Renard, *A. Ch.* [6] 1, 229; *cf.* Pelletier a. Walter, *A. Ch.* [2] 67, 99).

***n*-Cumene** C_6H_5Pr. *n-Propyl-benzene.* (158·5°). S.G. $^{\underline{0}}$ ·88 (Spica, *G.* 8, 408); $\frac{9\cdot8}{4}$ ·8702 (Schiff). C.E. (9·8 to 158·5) ·001184. V.D. 4·14 (for 4·14). S.V. 161·8 (Schiff, *A.* 220, 93).

Formation.—1. From *n*-propyl bromide,

bromo-benzene, and sodium (Fittig, Schäffer a. Konig, *A.* 149, 324).—2. From benzyl chloride and $ZnEt_2$ (Paternò a. Spica, *G.* 7, 21).—3. From Al_2Cl_6, benzene and allyl chloride (Wispek a. Zuber, *A.* 218, 378); according to Silva (*Bl.* [2] 43, 318) the product is isopropyl-benzene.—4. A product of the action of ethylidene chloride on toluene in presence of Al_2Cl_6 (Anschutz a. Romig, *B.* 18, 665).

Reactions.—1. In CS_2 solution it combines with CrO_2Cl_2, forming a chocolate pp. $PhPr2CrO_2Cl_2$ converted by water into phenyl-propionic aldehyde (Etard, *A. Ch.* [5] 22, 252). 2. *Chromic* mixture gives benzoic acid.—3. By the action of *bromine* (1 mol.) in the dark or in presence of 3 p.c. of iodine in diffused daylight, a mixture of *o*- and *p*-bromo-propyl-benzene $C_6H_4Br(C_3H_7)$ is obtained. By the action of bromine (1 or 2 mols.) in direct sunshine, the side chain is substituted in the β-position giving $C_6H_5.CHBr.CH_2.CH_3$ or $C_6H_5.CBr_2.CH_2.CH_3$. If the β-mono-bromo-propyl-benzene is treated at 100° in the dark with another mol. of bromine, αβ-di-bromo-propyl-benzene is produced $C_6H_5.CHBr.CHBr.CH_3$ [65·5°] (Schramm, *B.* 18, 1274).

References.—BROMO-CUMENE, CHLORO-CUMENE, NITRO-CUMENE, &c. *V.* also AZO- and HYDRAZO-COMPOUNDS.

ψ-CUMENE CARBOXYLIC ACID *v.* CUMINIC ACID.

ψ-CUMENE-SULPHONIC ACID $C_6H_2Me_3(SO_3H)$ [1:3:4:2]. Obtained by debromination of di-bromo-pseudo-cumene-sulphonic acid $C_6Me_3Br_2(SO_3H)$ [1:3:4:5:6:2] by the action of zinc-dust and aqueous NH_3 upon the sodium salt. It is formed, together with the isomeride (1:3:4:5) and other products, by the prolonged action of conc. H_2SO_4 upon durene (*q.v.*) or its mono-sulphonic acid.—NaA′: very soluble small flat needles or plates.

Amide $C_6H_2Me_3(SO_2NH_2)$: [113°]; small flat needles or plates; v. e. sol. alcohol (Jacobson, *B.* 19, 1222).

ψ-Cumene-sulphonic acid $C_6H_2Me_3(SO_3H)$ [1:3:4:5]. Obtained by debromination of bromo-pseudocumene-sulphonic acid by the action of zinc-dust and aqueous NH_3 upon the sodium salt (Jacobsen, *B.* 19, 1218), or by sodium-amalgam (Kelbe a. Pathe, *B.* 19, 1556). It is formed, together with the isomeride [1:3:4:2] and other products, by the prolonged action of conc. H_2SO_4 upon durene (*q. v.*) or its mono-sulphonic acid.

Salts.—NaA′aq: needles, v. sol. hot water.—KA′aq: similar to the preceding.—AgA′aq: sparingly soluble white plates.—BaA′aq: plates, sparingly sol. cold water (K. a. P.).—BaA′₂: thin prisms; sol. hot water, sl. sol. cold (J.).

Amide $C_6H_2Me_3(SO_2NH_2)$: [172°] (J.); [179°] (K. a. P.); needles or very small prisms; v. sol. alcohol.

ψ-Cumene sulphonic acid $C_6H_2Me_3SO_3H$ [1:2:4:5]. [112°]. Formed by dissolving ψ-cumene in conc. H_2SO_4 at 80°, and crystallised from dilute H_2SO_4 (Jacobsen, *A.* 184, 199). Cubes, sl. sol. dilute H_2SO_4. Converted by potash-fusion into $C_6H_2Me_2(OH)CO_2H$, whence, by distillation with lime, *m*-xylenol $C_6H_3Me_2(OH)$ [1:3:4] is got. Fusion of the K salt with sodium formate gives $C_6H_2Me_3.CO_2K$ (Reuter, *B.* 11, 29). By the action of bromine upon the aqueous solution 76 p.c. is converted into bromo-pseudo-cumene $C_6H_2Me_3Br$ [1:2.4:5], the remainder yielding bromo-pseudo-cumene-sulphonic acid $C_6HMe_3Br.SO_3H$ [1:2:4:3:5] (Kelbe a. Pathe, *B.* 19, 1546).

Salts.—NaA′ 5aq: transparent plates, loses 4aq in the air.—NaA′aq: white plates (from conc. solution).—KA′aq: sparingly soluble prisms.—AgA′aq: sparingly soluble needles.—BaA′₂. S. 4·5 at 11·5° (J.).—BaA′₂aq (Fittig a. Ernst, *A.* 139, 188).

Chloride $C_6H_2Me_3SO_2Cl$. [61°]. Monoclinic prisms (from ether).

Amide $C_6H_2Me_3SO_2NH_2$. [176°] (K. a. P.); [181°] (Jacobsen, *B.* 19, 2513). S. ·014 at 0°; ·26 at 100°. Large prisms, sol. hot, sl. sol. cold alcohol. Conc. HCl at 176° splits it up into NH_3, H_2SO_4, and ψ-cumene. Potassium permanganate gives $C_6H_2(CO_2H)Me_2(SO_2NH_2)$ [1:2:4:5], $C_6H_2(CO_2H)_2Me(SO_2NH_2)$ [1:4:2.5], and finally $C_6H_2(CO_2H)_3(SO_2NH_2)$ (Jacobsen a. H. Meyer, *B.* 16, 190). By heating with a small quantity of HCl there is formed $(C_6H_2Me_3SO_2)_2NH$ [177°], which is soluble in alkalis.

Cumene-(α)-sulphonic acid $C_6H_4(C_3H_7).SO_3H$. *Isopropyl-benzene sulphonic acid.* Formed in largest quantity by sulphonating cumene in the cold. By warming to 100°, or by several weeks' standing with the excess of H_2SO_4 it is in great part converted into the (β)-acid (Claus a. Tonn, *B.* 18, 1239). Small deliquescent scales. Potassium permanganate in presence of KOH forms $(CH_3)_2C(OH).C_6H_4.SO_3H$ (R. Meyer, *A.* 219, 300)

Salts.—KA′.—BaA′₂aq: laminæ. S. 4·6 at 16°, 5·6 at 60°, 50 at 100°.—PbA′₂aq: pearly scales.—CaA′₂ 2aq.—SrA′₂ 2aq. S. 100. On heating the solution saturated in the cold to 100° a crystalline pp. of SrA′₂ is formed.—MgA′₂ 7aq.—AgA′.

Amide $C_6H_4Pr.SO_2NH_2$. [108°] (M.; Spica, *G.* 9, 433); [112°] (C. a. T.). Converted into *p*-oxy-benzoic acid by treatment with $KMnO_4$ and fusion of the product with potash.

Cumene-(β)-sulphonic acid $C_6H_4(C_3H_7)SO_3H$. Formed, together with a smaller quantity of the (α)-sulphonic acid, by heating cumene with an excess of ordinary H_2SO_4 on the water-bath (Claus a Tonn, *B.* 18, 1239; Spica, *G.* 9, 133). Small needles. V. sol. water. By fusion with sodium formate it is converted into a cuminic acid which gives phthalic acid on oxidation (Claus a. Schulte, *B.* 19, 3012).

Salts.—A′₂Ba 3½aq: small needles; S 20 at 16°; more soluble than the Ba salt of the preceding acid.—A′₂Pb 2aq: easily soluble microscopic needles.—A′₂Mg 8aq: soluble pearly plates.—A′₂Zn 7aq: easily soluble glistening needles.—A′₂Cu 8aq: easily soluble large green needles.

Chloride $C_9H_{11}.SO_2Cl$: yellow oil.

Amide $C_9H_{11}.SO_2NH_2$: [127° uncor.] (C. a. T.); [96°] (S.); glistening needles.

***n*-Cumene sulphonic acid** $C_6H_4Pr\,SO_3H$. From *n*-cumene and H_2SO_4. According to Paternò a. Spica (*G.* 8, 408) both the *o* and *p* acids are formed.

Salts.—KA′½aq (from alcohol).—CaA′₂.—BaA′₂ (Fittig, *A.* 149, 330).

Amide $C_6H_4Pr\,SO_2NH_2$. [110°]. Scales (from water) (R. Meyer, *A.* 219, 298).

ψ-CUMENOL $C_6H_2(CH_3)_3OH$[5:4:2:1]. [72°]. (235°). H.F. p. 68,510 (Stohmann, *J. pr.* [2] 34, 818).

Formation.—1. Formed by diazotising ψ-cumidine [62°] and boiling the diazo- compound with water (Liebermann a. Kostanecki, *B.* 17, 885; Auwers, *B.* 17, 2976; Krohn, *B.* 21, 881). 2. By fusing ψ-cumene sulphonic acid with KOH (Reuter, *B.* 11, 29).

Properties.—Slender flexible needles, very volatile with steam. Insol. cold water. Fe_2Cl_6 does not colour its solutions. Gives a bromo-derivative [32°] and a di-bromo-derivative [150°].

Benzoyl derivative $C_6H_2Me_3(OBz)$. [63°]. H.F. 87,240 (Stohmann, *J. pr.* [2] 36, 8).

Methyl ether $C_6H_2(CH_3)_3OMe$. (214°) (H.); (211°) (Auwers, *B.* 18, 2657); colourless liquid. Formed by heating sulphate of diazo-pseudo-cumene with methyl-alcohol (Hofmann, *B.* 17, 1918).

Ethyl ether $C_6H_2(CH_3)_3OEt$: (224°); colourless liquid. Formed by heating sulphate of diazo-pseudo-cumene with ethyl-alcohol.

Isoamyl ether $C_6H_2(CH_3)_3OC_5H_{11}$: (265°).

Sulphate $C_6H_2Me_3(OSO_3H)$. From ψ-cumenol and H_2SO_4 (Reuter, *B.* 11, 29). Small crystals; decomposed by water into ψ-cumenol and H_2SO_4 even in the cold.—BaA'_2: slightly soluble leaflets. KA'.—ZnA'_2.

ψ-Cumenol $C_6H_2Me_3(OH)$[1:3:4:2]. [62°]. (233°). Formed from pseudo cumene-sulphonic acid (1:3:4:2) by KOH fusion (Jacobsen, *B.* 19, 1223). Long needles (from ether). Fe_2Cl_6 gives no colouration.

ψ-Cumenol $C_6H_2Me_3(OH)$. [95°]. (231° i.V.). From the corresponding cumidine [36°] by diazo-reaction (Edler, *B.* 18, 630). Formed also by fusing the corresponding sulphonic acid with potash (Jacobsen, *B.* 19, 1219). Long prisms. Gives no colour with Fe_2Cl_6. It gives a di-bromo-derivative [152°].

ψ-Cumenol $C_6H_2Me_3(OH)$. (217°). From the diazo- compound of ψ-cumidine (224°) by boiling with dilute H_2SO_4 (Engel, *B.* 18, 2230). Oil. Gives no colouration with Fe_2Cl_6.

o-**Cumenol** $C_6H_4Pr.OH$. *o-Isopropyl-phenol.* [15°]. (212° i.V.). S.G. $\frac{0}{4}$ 1·0124. From *o*-cumidine by displacing NH_2 by OH through the diazo- reaction (Fileti, *G.* 16, 113). Formed also by potash-fusion from cumene *o*-sulphonic acid (Spica, *G.* 9, 433). Its aqueous solution is coloured violet by Fe_2Cl_6. It gives a bromo- and a tri-nitro- derivative. Sodium and CO_2 gives cumenol carboxylic acid and di-oxy-di-isopropyl-diphenyl-carboxylic acid. PBr_5 gives bromo-cumene and $(C_6H_4PrO)_3PO$ (c 378 at 280 mm.), whence alcoholic KOH forms $(C_6H_4PrO)_2(HO)PO$.

Acetyl derivative C_6H_4PrOAc. (229°). S.G. 1·03. Liquid, decomposed by prolonged boiling with water.

Methyl ether C_6H_4PrOMe. (199° cor.).

Ethyl ether C_6H_4PrOEt. (209° cor.). S.G. $\frac{0}{4}$ ·9414.

p-**Cumenol** $C_6H_4Pr(OH)$ [1:4]. [61°]. (229° cor.). From cumene *p*-sulphonic acid by potash-fusion (Paternò a. Spica, *G.* 6, 535). Formed also by heating $C_6H_3(CO_2H)Pr(OH)$ [1:3:6] with conc. HCl at 180° (Jesurun, *B.* 19, 1416). Fe_2Cl_6 colours the alcoholic solution green.

Acetyl derivative C_6H_4PrOAc. (244° cor.). S.G. ^{0} 1·026.

Methyl ether $C_6H_4Pr.OMe$. (213° cor.). S.G. ^{0} ·962.

Ethyl ether $C_6H_4Pr.OEt$. (245°). S.G. ^{0} 1·026.

o-n-**Cumenol** $C_6H_4Pr(OH)$[1:2]. *o-Propyl-phenol.* (c. 225° cor.). S.G. ^{0} 1 015. From allyl iodide and phenol in presence of zinc and aluminium foil (P. F. Frankland a. T. Turner, *C. J.* 43, 358): $C_6H_5OH + C_3H_5I = HI + C_3H_5.C_6H_4OH$ and $C_3H_5.C_6H_4OH + 2HI = C_3H_7\,C_6H_4OH + I_2$. Formed also by fusing the corresponding sulphonic acid with potash (Spica, *G.* 8, 418). Liquid; its aqueous solution is turned violet by Fe_2Cl_6. CO_2 acting on its sodium derivative at 140° gives *o*-oxy-propyl-benzoic acid.

Methyl ether $C_6H_4Pr.OMe$. (208° cor.). S.G. ^{0} ·9694.

m-n **Cumenol** $C_6H_4Pr(OH)$[1:3]. [26°]. (228° i.V.). From oxy-*n*-cuminic acid and conc. HClAq at 190° (Jacobsen, *B.* 11, 1062). Crystals, v. sl. sol. water. Fe_2Cl_6 colours its alcoholic solution green.

p-n-**Cumenol** $C_6H_4Pr(OH)$[1:4]. (231° cor.). S.G. ^{0} 1·009. Formed by fusing the corresponding *n*-cumene sulphonic acid with potash (Spica, *G.* 8, 411). Formed also by diazotising amido-propyl-benzene and boiling the product with water (Louis, *B.* 16, 109). Oil. Sl. sol. cold water, v. sol. alcohol and ether. Fe_2Cl_6 gives at first a violet and then a permanent green colouration. CO_2 on the Na derivative gives *p*-oxy-*n*-cuminic acid.

Acetyl derivative $C_6H_4Pr(OAc)$. (243° cor.). S.G. ^{0} 1·029; ^{100} ·942.

Methyl ether $C_6H_4Pr(OMe)$. (215° cor.). S.G. ^{0} ·964; ^{100} ·912. Yields anisic acid on oxidation.

The same ether appears to be formed, together with anisole, by the action of boron-fluoride on anethol (Landolph, *B.* 13, 115).

Isomerides of cumenol *v.* MESITOL and HEMIMELLITHOL.

Derivatives of cumenol *v.* AMIDO-CUMENOL, BROMO-CUMENOL, NITRO-CUMENOL, &c.

Di-cumenol *v.* DI-OXY-DI-CUMYL.

CUMENOL-CARBOXYLIC ACID *v.* OXY-CUMINIC ACID.

CUMENOL SULPHONIC ACID $C_6H_3Pr(OH)(SO_3H)$. From cumenol and H_2SO_4 (Jacobsen, *B.* 11, 1062). The Ba salt forms crystalline crusts. Its solution is coloured violet by Fe_2Cl_6.

CUMENYL. A name sometimes applied to the radicle cumyl C_9H_{11}.

CUMENYL-ACRYLIC ACID *v.* CUMYL-ACRYLIC ACID.

CUMIC *v.* CUMINIC.

CUMIDIC ACID *v.* XYLENE DICARBOXYLIC ACID.

o-**CUMIDINE** $C_9H_{13}N$ *i.e.* $C_6H_4Pr(NH_2)$[1:2]. (215°). Formed by distilling amido-cuminic acid with baryta (Fileti, *G.* 13, 379). Formed also, together with the following, by nitrating cumene and reducing the product (Constam a. Goldschmidt, *B.* 21, 1157). Converted by passing over red-hot PbO into indole.

Salts.—B'HCl: large prisms.—$B'H_2C_2O_4aq$: [173°]; long prisms.

Acetyl derivative $C_9H_{11}NHAc$. [72°]. Tufts of needles.

p-**Cumidine** $C_6H_4Pr(NH_2)$[1:4]. (225°) (N.); (219°) (C. a. G.). S.G. ·953. Formed by reducing nitro-cumene (from cuminic acid) (Nicholson, *A.* 65, 58). From aniline, isopropyl alcohol, and $ZnCl_2$ at 270° (Louis, *B.* 16, 111). May be solidified by cold. — B'HCl. — $B'_2H_2PtCl_6$. — $B'HNO_3$.—$B'_2H_2SO_4$.—$B'_2C_2N_2$: long needles (Hofmann, *A.* 66, 145). Oxalate $B'_2H_2C_2O_4$ 2aq: [159°] (Constam a. Goldschmidt, *B.* 21, 1157).

Acetyl derivative $C_9H_{11}NHAc$ [102°].

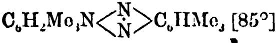
ψ-Cumidine $C_6H_2Me_3(NH_2)$[1:3:4:5]. [36°]. Formed by reduction of nitro-(pseudo)-cumene [20°] (Edler, *B.* 18, 630). Colourless crystals. Easily volatile with steam.

Salts.—B'HCl: fine felted needles.—$B'HNO_3$: small glistening plates. The oxalate and sulphate are sparingly soluble in cold water.

Acetyl derivative [194°]; long prisms; nearly insol. ether.

ψ-Cumidine $C_6H_2Me_3(NH_2)$[1:2:4:5]. [68°] (Auwers, *B.* 18, 2661); [63°] (H.). (235°). Crystalline solid.

Formation.—1. Occurs in the crude cumidine obtained by heating xylidine hydrochloride with methyl alcohol at a high temperature under pressure (Hofmann a. Martius, *B.* 4, 747; 13, 1730; Hofmann, *B.* 15, 2895; *cf.* Nolting a. Forel, *B.* 18, 2680).—2. By nitration and reduction of pseudocumene (Schaper, *Z.* 1867, 13). Large prisms. Nitrous acid converts it into $C_6H_2Me_3.N_2.C_6HMe_3(NH_2)$, whence may be obtained $C_6H_2Me_3.N_2.C_6HMe_3N_2Br_3$ [124°], $C_6H_2Me_3.N_2.C_6HMe_3.N_3$ [91°],


$C_6H_2Me_3N{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6HMe_3$ [85°] and

$C_6H_2Me_3.N_2.C_6HMe_3.N_2H$ [153°] (Zincke a. Jaencke, *B.* 21, 516).

Salts.—B'HCl: thick prisms, sol. water, sl. sol. dilute HCl. - $B'_2H_2Cl_2PtCl_4$: fine needles, decomposed by boiling water (De Coninck, *Bl.* [2] 45, 131).—$B'_2H_2SnCl_4$: laminæ.—$B'H_3PO_4$ (Lewy, *B.* 19, 2729).

Acetyl derivative $C_6H_2Me_3.NHAc$: [164°]; (360°); thick white needles; v. sol. alcohol and acetic acid, insol. water (Auwers, *B.* 18, 2661; *cf.* Nölting a. Baumann, *B.* 18, 1115).

Formyl derivative $C_6H_2Me_3.NH.COH$: [121°]; colourless prisms; v. sol. alcohol and ether, nearly insol. water.

Thioformyl derivative $C_6H_2Me_3.NH.CSH$. Formed by heating the formyl derivative with P_2S_5 (Senier, *B.* 18, 2296).

ψ-Cumidine $C_6H_2Me_3.NH_2$. (224°).

Preparation.—The solid hydrochloride obtained by adding conc. HCl to crude coml. cumidine is basified with NaOH and fractionated. The fraction c. 225°–227° is boiled with acetic acid for twelve hours, and the product crystallised from alcohol; a small quantity of acetylmesidine crystallises out, and the mother-liquors contain the acetyl derivative of the new cumidine, which is obtained pure by several crystallisations from water, and finally converted into the base by saponification with solid KOH.

Salts.—B'HCl: white needles; v. sol. water, nearly insol. conc. HCl. The platino-chloride is insol. water, sl. sol. alcohol. The nitrate is less soluble than the sulphate.

Acetyl derivative $C_6H_2Me_3.NHAc$: [112°]; crystalline solid (Engel, *B.* 18, 2229).

Cumidine $C_6H_2Me_3(NH_2)$[1:2:3:4]? *Hemimellithidine?* *Amido-c-tri-methyl-benzene.* (240°). From *o*-xylidine hydrochloride and MeOH at 310° (Nölting a. Forel, *B.* 18, 2680). Liquid.

Acetyl derivative $C_6H_2Me_3(NHAc)$. [above 180°].

ψ-Cumidine $C_6H_2Me_3.NH_2$[1:3:4:2]. (236° uncor.). Liquid at −15°. Obtained from nitro-ψ-cumidine (from tri-nitro-ψ-cumene) by elimination of the NH_2 group by the diazo- reaction and reduction of the nitro-ψ-cumene [30°], which is obtained with $SnCl_2$ (Mayer, *B.* 20, 971). Probably identical with the ψ-cumidine obtained by Nolting and Forel (*B.* 18, 2680) by nucleal methylation of the *o*-xylidine $C_6H_3Me_2NH_2$[2:3:1].

Acetyl derivative $C_6H_2Me_3(NHAc)$. [186°].

n-**Cumidine** *v.* Amido-phenyl-propane, vol. i. p. 179.

Isomeride of cumidine *v.* Phenyl-propylamine.

CUMILIC ACID $C_{20}H_{24}O_3$ *i.e.* $(C_6H_4(C_3H_7))_2C(OH).CO_2H$? [120°]. Prepared by fusion of cuminil with KOH; yield 70 p.c. (Bosler, *B.* 14, 326). Fine white needles. Sol. alcohol, ether, and benzene, sl. sol. water.

CUMINAL-ACETONE *v.* Methyl propyl-styryl ketone.

Di-cuminal-acetone *v.* Di-propyl-di-styryl ketone.

CUMINDIGO *v.* Di-isopropyl-indigo.

CUMINIC ALCOHOL *v.* Cuminyl alcohol.

o-*n*-**CUMINIC ACID** $C_{10}H_{12}O_2$ *i.e.* $C_6H_4Pr(CO_2H)$ [1:2]. *o-n-Propyl-benzoic acid.* Mol. w. 164. [58°]. From phthalyl-propionic acid, conc. HIAq (10 pts.), and red phosphorus (1 pt.) (Gabriel a. Michael, *B.* 11, 1014). Slender leaflets.

p-*n*-**Cuminic acid** $C_6H_4.Pr(CO_2H)$ [1:4]. *p-n-Propyl-benzoic acid* [140°].

Formation.—1. From *p*-bromo-*n*-propylbenzene, sodium, and CO_2 (R. Meyer, *J. pr.* [2] 34, 102).—2. From C_6H_4PrPr by oxidation (Paternò a. Spica, *B.* 10, 1716).—3. From $C_6H_4Pr_2$ and dilute HNO_3 (H. Körner, *A.* 216, 228).

Properties.—Laminæ (from water) or needles (from dilute alcohol). Sl. sol. boiling water. Volatile with steam. $KMnO_4$ gives terephthalic acid.

Salts.—CaA'_2 3aq: slender satiny needles.—SrA'_2 2½aq.—BaA'_2 2aq.—PbA'_2 2aq.- AgA'.

Nitrile $C_6H_4Pr.CN$. [227°]. From *p*-propylphenyl thiocarbimide and copper powder at 220° (Francksen, *B.* 17, 1229). Liquid. Saponified by conc. HClAq at 200°.

o-**Cuminic acid** $C_6H_4Pr.CO_2H$ [1:2]. Formed by fusing a salt of cumene-(β)-sulphonic acid with an excess of sodium formate; the yield is 10 p.c. Sublimable. Volatile with steam. V. sol. alcohol, ether, &c., insol. cold water. Oxidation with $KMnO_4$ gives *o*-phthalic acid. Its alkaline salts are excessively soluble.—A'Ag: insoluble white pp.—A'_2Ca 2aq: small soluble needles.—A'_2Ba 2aq: soluble needles.—A'_2Mg 6aq: very soluble needles.—A'_2Pb aq: very sparingly soluble white powder.—A'_2Cu 2½aq: very sparingly soluble blue-green amorphous pp.

Chloride $C_6H_4Pr.COCl$: yellowish oil, v. sol. ether and chloroform.

Amide $C_6H_4Pr.CO.NH_2$: [124° uncor.]; small needles; v. sol. alcohol and ether, v. sl. sol. water (Claus a. Schulte im Hof, *B.* 19, 3013).

p-Iso-**cuminic acid** $C_6H_4Pr(CO_2H)$ [1:4]. [117°] (M.). H.C.v. 1,239,000 (Berthelot a. Louguinine, *A. Ch.* [6] 13, 333).

Formation.—1. From bromo-iso-propyl-benzene, Na, and CO_2 (R. Meyer, *J. pr.* [2] 31, 100).—2. By the oxidation of cuminic aldehyde or oil of cumin (Gerhardt a. Cahours, *A. Ch.* [3] 1, 70; Beilstein a. Kupffer, *B.* 6, 1184; *A.* 170, 302; Lippmann a. Lange, *B.* 13, 1660; Meyer, *A.* 219, 244).—3. Cymene when taken internally passes into the urine as cuminic acid (Nencki a. Ziegler, *B.* 5, 749; *cf.* Hofmann, *A.* 74, 342).

Properties.—From water (3 pts.) and alcohol (1 pt.) it separates in triclinic needles: $a:b:c = {\cdot}6742:1:{\cdot}8072$; $\alpha = 86° \ 55'$, $\beta = 101° \ 12'$, $\gamma = 106° \ 55'$ (Groth; *cf.* Panebianco, *G.* 10, 81). V. sl. sol. cold water, v. sol. alcohol and ether. Converted into cumene by distillation over lime. Chromic mixture oxidises it to terephthalic acid. $KMnO_4$ forms, as an intermediate product, oxy-propyl-benzoic acid $(CH_3)_2C(OH).C_6H_4.CO_2H$ (Meyer).

Salts.—BaA'_2 2aq: laminæ. S. ·996 at 20·5°.—CaA'_2 5aq: needles. S. ·81 at 20·5°.—MgA'_2 6aq: laminæ. S. ·825 at 20·5°.—AgA'.

Ethyl ether EtA'. (240°). V.D. 6·65.

Phenyl ether PhA'. [58°]. From potassium-phenol and the chloride of the acid (Williamson a. Scrugham, *Pr.* 7, 18). Also formed by distilling cuminyl-salicylic acid (Kraut, *J.* 1858, 406; *Ar. Ph.* [2] 96, 271).

Eugenyl ether $C_6H_3(C_3H_5)(OMe)A'$. Tables (Cahours, *A.* 108, 323; *A. Ch.* [3] 41, 191).

Anhydride $(C_6H_4Pr.CO)_2O$. Oil (Gerhardt, *A.* 87, 77; *A. Ch.* [3] 37, 304).

Peroxide $(C_6H_4Pr.CO)_2O_2$. Needles (from ether). Explodes when heated (Brodie, *P.* 121, 372; *Pr.* 12, 655).

Chloride $C_6H_4Pr.COCl$. (257°). S.G. ^{15} 1·07. Liquid (Cahours, *A.* 70, 45; *A. Ch.* [3] 23, 317).

Amide $C_6H_4Pr.CONH_2$. [154°] (F.); [c. 157°] (G.). *Formation.*—1. By heating ammonium cuminate (Field, *A.* 65, 49). 2. From the nitrile and alcoholic KOH.—3. From the anhydride and NH_3 (Gerhardt, *A.* 87, 167).—4. By heating cuminic acid (164 g.) with potassium sulphocyanide (50 g.) for 5 hours with inverted condenser at 210°, and then for 1 hour at 300°. The nitrile is formed at the same time (Fileti, *G.* 16, 281).—5. By the action of chloroformamide $OC(NH_2)Cl$ upon cumene in presence of Al_2Cl_6 (Gattermann a. Schmidt, *A.* 244, 54; *B.* 20, 860). *Properties.*—Biaxial crystals, insol. cold water, sl. sol. ether, v. sol. alcohol and hot benzene. When boiled with water and yellow HgO it forms $(C_6H_4Pr.CONH)_2Hg$ 1½aq, which crystallises in needles [190°].

Anilide $C_6H_4Pr.CONHPh$. Long satiny needles (from alcohol). Sl. sol. alcohol (Cahours, *A. Ch.* [3] 23, 349).

Benzene sulphamide $C_6H_4Pr.CO.NH.SO_2Ph$. [161°]. From cuminyl chloride and the amide of benzene sulphonic acid (Gerhardt a. Chiozza, *A. Ch.* [3] 46, 151). Prisms. $AgNO_3$ and a little NH_3 give needles of $C_6H_4Pr.CO.NAg.SO_2Ph$, which forms a crystalline compound with NH_3 (1 mol.). The benzoyl derivative $C_6H_4Pr.CO.NBz.SO_2Ph$ is formed as a crystalline mass by treating $AgNBz.SO_2Ph$ with cuminyl chloride.

o-Oxy-benzamide $C_6H_4Pr.CO.NH.CO.C_6H_4.OH$. From salicylamide and cuminyl chloride. Needles.

Nitrile $C_6H_4Pr.CN$. (244° i.V.). S.G. ^{14} ·765. Formed by heating the amide (Field, *Mem. Chem. Soc.* 3, 408; *A.* 65, 51), or by heating cuminic acid (2 mols.) with KCyS (1 mol.) (Letts, *B.* 5, 674; Fileti, *G.* 16, 282). Formed also by treating potassium cuminate with CyBr (Cahours, *A. Ch.* [3] 52, 201; *A.* 108, 326). Liquid, sl. sol. water, v. e. sol. alcohol and ether.

ψ-Cuminic acid $C_6H_2Me_3(CO_2H)$ [1:2:4.5]. *Durylic acid. Tri-methyl-benzoic acid.* [149°].

Formation.—1. By boiling durene with dilute HNO_3 (Jannasch, *Z.* 1870, 449) or with the calculated quantity of CrO_3 in HOAc (Gissmann, *A.* 216, 205).—2. By fusing potassium ψ-cumene sulphonate with sodium formate (Reuter, *B.* 11, 31).—3. From the nitrile (Nef, *A.* 237, 3).—4. By hydrolysis of its amide (*v. infra*).

Preparation.—Durene is boiled for 3 or 4 hours with dilute HNO_3 (1 vol. of HNO_3 (1·4 S.G.) to 3 vols. water). The product is filtered off, extracted with Na_2CO_3, and the solution precipitated with HCl. The crude acid is filtered off, treated with tin and HCl to remove nitro- compounds, and distilled with steam. The yield is 40–50 p.c. of the durene (Nef, *B.* 18, 2801).

Properties.—Needles (from benzene). V. sl. sol. boiling water, v. e. sol. alcohol and ether. Volatile with steam.

Salts.—CaA'_2 2aq. BaA'_2 7aq: prisms.

Amide $C_6H_2Me_3.CONH_2$. [201°]. From ψ-cumene and chloroformamide $Cl.CONH_2$ in presence of Al_2Cl_6 (Gattermann, *A.* 244, 51). Needles (from dilute alcohol).

Nitrile [58°]. (250°). Formed by the action of $CuSO_4$ and KCN upon diazo-pseudo-cumene (Haller, *B.* 18, 93). Long colourless needles. V. sol. alcohol, ether, benzene, and ligroin, insol. water.

(α)-Cuminic acid $C_6H_2Me_3(CO_2H)$ [1:2:3:5]. [216°]. (α)-*Isodurylic acid.* Formed together with the (β) and (γ) isomerides by oxidation of isodurene with HNO_3. Distillation with lime yields hemimellithol. — A'_2Ba 4aq: long fine needles. — A'Ca 5aq (Jacobsen, *B.* **15**, **1855**; Bielefeldt, *A.* 198, 384).

(β)-Cuminic acid $C_6H_2Me_3(CO_2H)$ [1:3:5:2]. (β)-*Isodurylic acid. Mesitylene carboxylic acid.* [151°]. Formed together with the (α) and (γ) isomerides by oxidation of iso-durene with HNO_3 (Jacobsen, *B.* 15, 1855). Distils without decomposition. Thick glistening prisms. On distillation with lime it gives mesitylene. CaA'_2 2aq: microscopic needles.

(γ)-Cuminic acid $C_6H_2Me_3(CO_2H)$ [1:2:4.6]. *ψ-Cumene carboxylic acid.* (γ)-*Isodurylic acid.* [85°]. Formed together with the (α)- and (β)-isomerides by oxidation of isodurene with HNO_3 (Jacobsen, *B.* 15, 1855). Distils without decomposition. Volatile with steam. Needles. Sol. alcohol, ether, and hot water, nearly insol. cold water. On distillation with lime it gives pseudo-cumene.

Salts.—$A'K^{x}$: extremely soluble amorphous solid. — A'_2Ba^{x}: uncrystallisable. — A'_2Ca 2aq: microscopic needles.

***c*-Cuminic acid** $C_6H_2Me_3(CO_2H)$[1:2:3:4]. *Tri-methyl-benzoic acid.* [168°]. Formed by oxidation of the consecutive tetra-methyl-benzene (prehnitene) by boiling for 12 hours with dilute HNO_3. Long glistening prisms. V. e. sol. hot alcohol. Volatile with steam. By distillation with lime it yields the consecutive tri-methyl benzene (hemimellithene) (Jacobsen, *B.* 19, 1214).

References. — AMIDO-CUMINIC ACID, BROMO-CUMINIC ACID, NITRO-CUMINIC ACID, OXY-CUMINIC ACID.

CUMINIC ALDEHYDE $C_{10}H_{12}O$ *i.e.* $C_6H_4(C_3H_7).CHO$ [1:4]. *Cuminol. Isopropyl-benzoic aldehyde.* Mol. w. 118. (237·5° cor.) (Schiff); (222° cor.) (Lippmann a. Strecker, *Sitz. W.* [2] 78, 570). S.G. $\frac{0}{}$ ·9832; $\frac{13.4}{}$ ·9727. V.D. 5·24 (calc. 5·13). Occurs, together with cymene, in oil of cumin (from *Cuminum Cyminum*), and in the volatile oil from the seeds of the water-hemlock (*Cicuta virosa*). It is separated from these oils by $KHSO_3$ (Gerhardt a. Cahours, *A. Ch.* [3] 1, 60; Bertagnini, *A.* 85, 275; Kraut, *A.* 98, 366; Trapp, *A.* 108, 386). Formed by boiling $C_3H_7.C_6H_4.CH_2Cl$ with lead nitrate and water (Errera, *G.* 14, 278). Formed also by treating cymene (1 mol.) with CrO_2Cl_2 (3 mols.) in CS_2, without cooling, and decomposing the product with water (Etard, *C. R.* 90, 534). The cuminic aldehyde (220°) so formed is perhaps identical with ordinary cuminic aldehyde. On oxidation it gives a cuminic acid [129°], whence potash-fusion gives *p*-toluic acid.

Properties.—Oil, smelling like oil of cumin. Oxidises in the air, becoming resinous.

Reactions. 1. Cold fuming HNO_3 gives *p*-iso-cuminic acid. Hot HNO_3 forms nitro-iso-cuminic acid.—2. *Chromic acid mixture* gives *p*-iso-cuminic and finally terephthalic acid. —3. Cl and Br act by substitution.—4. NH_3 forms hydrocumin-amide a thick liquid (Gerhardt a. Cahours; Borodin, *B.* 6, 1253). According to Uebel (*A.* 215, 303) it is a stellate mass [65°] which may be reduced by sodium amalgam to cuminyl-amine and di-cuminyl-amine, and is converted by dilute acids into NH_3 and cuminic aldehyde. Sieveking (*A.* 106, 357) could not obtain it. Aqueous NH_3 at 130° forms an isomeric base $C_{30}H_{36}N_2$ [205°] which forms a sparingly soluble sulphate [192°].—5. *Ammonium sulphide* forms $(C_{10}H_{12}S)_x$.—6. Boiling *aqueous* and *alcoholic potash* form cuminyl alcohol and *p*-iso-cuminic acid.—7. *Potash-fusion* gives *p*-iso-cuminic acid and cymene.—8. Heating with potassium forms $C_{10}H_{11}OK$(?) (Chiozza, *A.* 87, 302; *cf.* Church, *P. M.* [4] 25, 522).—9. In ethereal solution it is partly converted by treatment with *sodium amalgam* into the sodium derivative of hydrocuminoin $C_6H_4Pr.CH(OH).CH(OH).C_6H_4Pr$ [135°] (M. Wallach, *A.* 226, 78; *cf.* Claus, *A.* 137, 104).—10. *Acetamide* at 175° gives $C_6H_4(C_3H_7)CH(NHAc)_2$ [212°] (Raab, *B.* 8, 1150).—11. *Benzamide* gives in the same way $C_6H_4(C_3H_7)CH(NHBz)_2$ [224°] which crystallises from alcohol in needles, insol. water (R.). —12. *Ethylene-diamine* at 120° gives $(C_3H_7.C_6H_4.CH{:}N)_2C_2H_4$ [64°] (Mason, *B.* 20, 267). — 13. Hydrogen cyanide and HCl give $C_6H_4(C_3H_7).CH(OH).CO_2H$.—14. Distillation over $ZnCl_2$ gives cymene (Louguinine, *Z.* 1867, 351). 15. With butyric aldehyde and butyric anhydride it gives $C_3H_7.C_6H_4.CH{:}CEt.CO_2H$ (Perkin).

Combination.—$C_{10}H_{12}(OH)(SO_3Na)$ aq: needles, sol. water, insol. cold alcohol. ether, and aqueous $NaHSO_3$.

Di-methyl-amido-anilide $C_6H_4(C_3H_7).CH{:}N.C_6H_4(NMe_2)$: [99°]; small glistening crystals (from alcohol) (Nuth, *B.* 18, 573).

Oxim $C_{10}H_{12}.NOH$. [52°]. Formed by the action of hydroxylamine on cuminic aldehyde (Westenberger, *B.* 16, 2994). Sl. sol. water.

Derivatives of cuminic orthaldehyde.

Diacetyl derivative $C_6H_4(C_3H_7)CH(OAc)_2$. Obtained by the action of silver acetate on $C_6H_4(C_3H_7)CHCl_2$ (from cuminol and PCl_5). Crystals (Sieveking, *A.* 106, 258).

Di-benzoyl derivative $C_6H_4(C_3H_7).CH(OBz)_2$. [88°]. Needles (Tüttscheff, *A.* 109, 368).

Di-thymyl derivative $C_6H_4(C_3H_7).CH(OC_{10}H_{13})_2$. [157°]. From $C_6H_4(C_3H_7).CHCl_2$, thymol, and KOH (Engelhardt a. Latschinoff, *Z.* 1869, 43). Tables.

Cuminoin $C_{20}H_{24}O_2$ *i.e.* $C_6H_4(C_3H_7).C(OH)H.CO.C_6H_4(C_3H_7)$. [101°]. Prepared by boiling cuminic aldehyde with alcoholic KCN; the yield is about 45 p.c. (Bosler, *B.* 14, 323). Slender white needles; sol. alcohol, ether, and benzene, sl. sol. water and ligroin. It reduces Fehling's solution in the cold. Alcoholic KOH gives a violet colouration.

Acetyl derivative $C_{20}H_{23}O(OAc)$: [75°]; tables or prisms (Widmann, *B.* 14, 609).

Hydrocuminoin $C_3H_7.C_6H_4.CH(OH).CH(OH).C_6H_4.C_3H_7$. [135°].

Formation. -1. From cuminoin and sodium amalgam. -2. From cuminic aldehyde by treating its ethereal solution with sodium amalgam or with alcoholic HCl and zinc (Claus, *A.* 137, 101; Raab, *B.* 10, 54).—3. Its di-acetyl derivative is formed by heating cuminic aldehyde with NaOAc and Ac_2O at 160° (Widmann, *B.* 19, 256).

Properties.—Small needles (from dilute alcohol). Insol. water. Oxidised by conc. HNO_3 to cuminoin. Pentachloride of phosphorus gives $C_3H_7.C_6H_4.CHCl\ CHCl.C_6H_4.C_3H_7$ [185°].

Di-acetyl derivative $C_{20}H_{24}Ac_2O_2$. [144°].

Deoxy-cuminoin $C_3H_7.C_6H_4.CH_2.CO.C_6H_4.C_3H_7$. [58°]. From cuminic aldehyde by treatment with zinc and alcoholic HCl (B.). Slender laminæ (from dilute alcohol); v. sl. sol. water.

Cuminil $C_{20}H_{22}O_2$ *i.e.* $C_6H_4(C_3H_7).CO.CO.C_6H_4(C_3H_7)$. [84°]. Yellow prisms. Sol. alcohol, ether, and benzene, v. sl. sol. water. Distils undecomposed. Prepared by oxidation of cuminoin with chlorine. On fusion with caustic potash it gives rise to cumilic acid $(C_3H_7.C_6H_4)_2C(OH).CO_2H$ [120°] (Bösler, *B.* 14, 325).

Isocuminic aldehyde $C_{10}H_{12}O$. [80°]. (220°). Formed together with the liquid aldehyde by the action of water upon the compound $C_{10}H_{14}2CrO_2Cl_2$, obtained from cymene derived from turpentine (Etard, *A. Ch.* [5] 22, 259). Solid resembling camphor. Oxidised by the air to a cuminic acid [51°].

CUMINOL *v.* CUMINIC ALDEHYDE.

CUMINURIC ACID $C_{12}H_{15}NO_3$ *i.e.* [4:1]$C_6H_4(C_3H_7).CO.NH.CH_2.CO_2H$. [168°]. Occurs in the urine of animals who have been given doses of cymene (Jacobsen, *B.* 12, 1512). Prepared by the action of cuminyl chloride on glycocol-silver (Cahours, *A. Ch.* [3] 53, 356). Glistening scales or large plates. Insol. cold water, v.

sol. hot water and alcohol. On heating with HCl to 120° it decomposes into glycocol and cuminic acid [117°]

Salts. - BaA'_2 aq: leaflets or flat needles, S. ·45 at 6°. - CaA'_2 3aq: fine needles, sl. sol. cold water. KA′ and NaA′: very soluble fine needles.

DI-CUMINYL $C_{20}H_{26}$ *i.e.* $C_3H_7.C_6H_4.CH_2.CH_2.C_6H_4.C_3H_7$. (above 360°). From cuminyl chloride and sodium (Cannizzaro a. Rossi, *A.* 121, 251). Plates.

CUMINYL ALCOHOL $C_{10}H_{14}O$ *i.e.* $C_6H_4Pr.CH_2OH$ [4:1]. Mol. w 150. (217° cor.). S.G. ^{15} ·978. Formed, together with cuminic acid, by boiling cuminic aldehyde with alcoholic potash (Kraut, *A.* 92, 66; 192, 224; Fileti, *G.* 14, 498). Liquid, miscible with alcohol and ether. Boiling with zinc-dust converts it into *n*-cymene, the Pr changing to Pr. Boiling alcoholic KOH forms cuminic acid and cymene. Boiling with small quantities of dehydrating agents converts it into di-cuminyl oxide.

CUMINYL-AMIDO-PHENOL $HO.C_6H_4.NH.CH_2.C_6H_4Pr$. *Oxy-phenyl-cuminyl-amine.* [108°]. Formed by reducing with sodium amalgam the product obtained by the action of cuminol on amidophenol (Uebel, *A.* 245, 297). Greyish white plates. V. e. sol. alcohol, ether.

Salts. $C_{16}H_{17}NH(ONa)$. V. sol. water, giving a red solution.—B′HCl. White plates. V. sol. alcohol, hot water, m. sol. cold water.

Nitrosamine $C_{16}H_{17}OHN.NO$. Yellowish brown crystalline substance. V. sol. alcohol, ether.

CUMINYL-AMINE $C_{10}H_{15}N$ *i.e.* $C_6H_4(C_3H_7).CH_2.NH_2$ [1:4]. *Exo-amido-cumene. Isopropyl-benzyl-amine.* (226° at 724 mm.). Prepared by reduction of the oxim of cuminic aldehyde, $C_6H_4(C_3H_7).CH:NOH$ (5 pts.), with sodium amalgam (150 pts.) and acetic acid (12 pts.) in alcoholic solution at 40°–50°; the yield is good (Goldschmidt a. Gessner, *B.* 20, 2413). Formed also, together with di- and tri-cuminyl-amine, by heating cuminyl chloride with alcoholic NH_3 at 100° (Rossi, *C. R.* 51, 570; *A. Suppl.* 1, 141). Also from thio-cuminic amide $C_3H_7.C_6H_4.CS.NH_2$, zinc and alcoholic HCl (Czumpelik, *B.* 2, 185). Colourless liquid, of basic smell. Nearly insol. water. Absorbs CO_2 from the air, and solidifies to a crystalline carbamate.

Salts.—B′HCl: glistening colourless plates, v. sol. water and alcohol. - $B'_2H_2Cl_2PtCl_4$: nearly insoluble yellow pp.

Acetyl derivative $C_{10}H_{13}(NHAc)$: [65°]; pearly plates; v. sol. alcohol, ether, and benzene, sl. sol. hot water and hot ligroin.

Di-cuminyl-amine $(C_3H_7.C_6H_4)_2NH$. [168°]. (c. 290° at 100 mm.). Formed as above (R.). Formed also by the action of sodium amalgam on the product of the action of dry NH_3 on cuminic aldehyde (Uebel, *A.* 215, 309). Crystals, insol. water, v. sol. alcohol and ether. Forms a crystalline nitrosamine.

Salts. B′HCl: plates (from alcohol); v. sl. sol. cold, m. sol. hot, water, v. e. sol. alcohol. —$B'_2H_2PtCl_6$: yellow needles.

Tri-cuminyl-amine $(C_3H_7.C_6H_4)_3N$. [82°]. Formed as above (R.). Its hydrochloride forms needles, insol. water.

CUMINYL-CARBAMATE $NH_2.CO_2.CH_2.C_6H_4.C_3H_7$. [89°]. Formed, together with ω-chloro-cymene, by passing cyanogen chloride into cuminyl alcohol (Spica, *G.* 5, 394). Prisms, not volatile with steam. Sl. sol. cold, v. sol. hot, water.

CUMINYL CHLORIDE *v.* ω-CHLORO-CYMENE.

CUMINYL-ETHYL OXIDE $C_6H_4Pr.O.Et$. (227°). From ω-chloro-cymene and alcoholic KOH (Errera, *G.* 14, 282)

CUMINYLIDENE-ACETONE $CH_3.CO.CH:CH.C_6H_4Pr$. (181° at 23 mm.). From acetone (20 pts.), cuminic aldehyde (20 pts.), water (300 pts.), alcohol (170 pts.), and NaOH (2 pts.) in the cold (Claisen a. Ponder, *A.* 223, 147). Thick yellowish oil.

Di-cuminylidene-acetone $(C_6H_4Pr.CH:CH)_2CO$. [107°]. From cuminic aldehyde (20 pts.), acetone (4 pts.), water (300 pts.), alcohol (250 pts.), and NaOH (2 pts.), in the cold (C. a. P.). Long light-yellow prisms (from alcohol).

CUMINYLIDENE-AMIDO-PHENOL $HO.C_6H_4N:CH\,C_6H_4Pr$. [183°]. Formed by the action of amidophenol on an alcoholic solution of cuminol (Uebel, *A.* 215, 296). Green prismatic needles (from alcohol). Is converted by sodium amalgam into cuminyl amido-phenol.

CUMINYLIDENE CHLORIDE *v.* ωω-DI-CHLORO-CYMENE.

DI-CUMINYLIDENE-ETHYLENE-DIAMINE $C_{22}H_{28}N_2$ *i.e.* $C_2H_4(N:CH.C_6H_4Pr)_2$. *Di-isopropyl-benzylidene-ethylene diamine.* [64°]. Formed by heating ethylene diamine (1 mol.), with cuminic aldehyde (2 mols.) to 120°. Long white needles. Easily soluble in alcohol, benzene, chloroform, and petroleum-ether. Decomposed into its constituents by acids or by heating with water (Mason, *B.* 20, 270).

CUMINYLIDENE-DI-METHYL-*p*-PHENYLENE DIAMINE $Pr.C_6H_4CH:NC_6H_4NMe_2$. [100°]. Formed by the action of $Pr.C_6H_4.CHO$ on di-methylaniline (Uebel, *A.* 245, 299). Lemon-yellow needles. V. sol. alcohol and ether, insol. water. Is decomposed by acids or alkalis into its components.

CUMINYL-DI-METHYL-*p*-PHENYLENE DIAMINE $Pr.C_6H_4.CH_2.NH.C_6H_4.NMe_2$. [39°]. Formed by reducing cuminylidene-di-methyl-*p*-phenylene-diamine with sodium amalgam in an alcoholic solution (Uebel, *A.* 245, 300). Colourless prismatic plates. V. e. sol. alcohol and ether. Gives a nitroso- derivative [87°], crystallising in yellow needles. The hydrochloride is v. sol. water, v. e. sol. alcohol, and sl. sol. ether.

DI-CUMINYL OXIDE $C_{20}H_{26}O$ *i.e.* $(C_6H_4Pr.CH_2)_2O$. (350°).

Formation. - 1. From $C_6H_4Pr.CH_2ONa$ and $C_6H_4Pr.CH_2Cl$ (Fileti, *G.* 14, 496).—2. By distilling cuminyl alcohol with dilute H_2SO_4.—3. One of the products of the action of alcoholic potash on cuminic aldehyde.

Properties.—Oil. Boils at 350° with partial decomposition into cuminic aldehyde and cymene.

CUMINYL-PHENOL $C_{16}H_{18}O$ *i.e.* $C_3H_7.C_6H_4.CH_2.C_6H_4OH$. (300°) at 60 mm. Formed by treating a mixture of phenol and cuminyl alcohol with HOAc and H_2SO_4 (Paternò a. Fileti, *G.* 5, 383).

CUMINYL THIOCARBIMIDE $C_6H_4Pr.CH_2NCS$. (245°–270°). From di-cuminyl-thio-urea and P_2O_5 (Raab, *B.* 10, 52).

CUMINYL-THIO-UREA $C_6H_4(C_3H_7).CH_2.NH.CS.NH_2$ [1:4]. *Propyl-benzyl-thio-urea.* [c. 110°]. Formed by mixing solutions of ammonium sulphocyanide and cumyl-amine hydrochloride, and evaporating to dryness. Colourless plates (Goldschmidt a. Gessner, *B.* 20, 2416).

Di-cuminyl-thio-urea $\{C_6H_4(C_3H_7).CH_2.NH\}_2CS$ [1:4]. *Di-p-propyl-di-benzyl-thio-urea.* [128°]. Formed by the action of alcoholic sulphide of carbon upon cumylamine $C_6H_4(C_3H_7).CH_2.NH_2$. Glistening needles (Raab, *B.* 10, 53; Goldschmidt a. Gessner, *B.* 20, 2115).

CUMINYL-UREA $C_{11}H_{16}ON_2$ *i.e.* $C_6H_4(C_3H_7).CH_2.NH.CO.NH_2$ [1:4]. *Propyl-benzyl-urea.* [135°]. Formed by warming a solution of cumylamine hydrochloride with potassium cyanate. Slender white needles (from hot water) (Raab, *B.* 8, 1151; Goldschmidt a. Gessner, *B.* 20, 2414).

Di-cuminyl-urea $(C_3H_7.C_6H_4.CH_2.NH)_2CO$. [122°]. From cuminyl cyanate and cuminyl amine (Raab, *B.* 10, 52). Small needles.

CUMONITRILE *v. Nitrile of* CUMINIC ACID.

CUMOPHENOL *v.* CUMENOL.

CUMOQUINOLINE *v.* (*iso*)-PROPYL-QUINOLINE.

ψ-CUMOQUINONE $C_6HMe_3O_2$ [2:3:5:4:1]. [11°]. Formed by oxidising isoduridine $C_6HMe_4(NH_2)$ [2:3:5:4:1]. Needles (from water). Liquid above 11°. Reduced by SO_2 to hydro-cumoquinone $C_6HMe_3(OH)_2$ [169°] (Nolting a. Baumann, *B.* 18, 1152).

ψ-CUMOQUINONE CARBOXYLIC ACID $C_6Me_3O_2.CO_2H$ (1:3:4:2:5:6). [128°]. Formed by oxidising an aqueous solution of the chloride of di-amido-tri-methyl-benzoic acid with Fe_2Cl_6 (Nef, *A.* 237, 11). Golden yellow needles. V. sol. alcohol, ether, chloroform, m. sol. petroleum ether.

Reactions.—Liberates CO_2 from carbonates; sol. alkalis and ammonia with yellow colour. Hydroxylamine yields an unstable quinone oxim. HNO_3 (1.4) yields nitro-tri-methyl-quinone. Reduced by zinc-dust and aqueous NaOH to di-oxy-tri-methyl-benzoic acid. The Ag, Pb, Ba, and Cu salts are all yellow.

Ethyl ether $C_6O_2Me_3CO_2Et$. [51°]. Yellow needles. V. sol. alcohol and ether, m. sol. ligroin.

CUMOSTYRIL *v.* (*Py.* 3)-OXY-(*B.* 3)-ISOPROPYL-QUINOLINE.

CUMYL. This name is sometimes given to the radicles cuminyl $C_9H_{11}.CH_2$ and cuminoyl $C_9H_{11}.CO$, but it is used in this dictionary to denote the radicle C_9H_{11}; cumyl being propyl-phenyl, while ψ-cumyl is *u*-tri-methyl-phenyl.

CUMYL-ACRYLIC ACID $C_{12}H_{14}O_2$ *i.e.* $C_6H_4(C_3H_7)CH{:}CH.CO_2H$ [4:1]. *Isopropyl-cinnamic acid.* [158°]. From cuminic aldehyde, NaOAc, and Ac_2O (Perkin, *C. J.* 31, 388; Widmann, *B.* 19, 255). Needles (from alcohol). V. sol. alcohol and HOAc, sl. sol. boiling water. Split up by heat into CO_2 and isopropyl-styrene. Aqueous CrO_3 gives cuminic aldehyde. Sodium amalgam gives *β-n*-cumyl-propionic acid.

Salts.—*NH_4A': asbestos-like crystals, m. sol. water.—CaA'_2: needles, sl. sol. water; absorbs oxygen at 100°.—SrA'_2 2aq.—AgA': bulky pp.

Chloride $C_6H_4Pr.CH{:}CH.COCl$. [c. 25°].

Amide $C_6H_4Pr.CH{:}CH.CONH_2$. [186°].

Derivatives *v.* AMIDO-, NITRO-, and OXY-CUMYL-ACRYLIC ACID.

Di-bromide $C_6H_4(C_3H_7).CHBr.CHBr.CO_2H$. [190°]. Small white balls. Sparingly sol. in hot benzene (Widmann, *B.* 19, 258).

ψ-CUMYL-AMIDO-CROTONIC ACID $Me_3C_6H_2NH.C(Me){:}CHCO_2Et$. Formed by the action of acetoacetic ether on $C_6H_2Me_3(NH_2)$ [1:2:4:5] (Conrad a. Limpach, *B.* 21, 528). Viscous mass. Yields on distillation di-cumyl-urea and a quinoline derivative.

Methyl ether MeA'. [60°]. Formed by the action of methyl acetoacetate on ψ-cumidine (Conrad a. Limpach, *B.* 21, 528). White crystals (from alcohol). Yields a quinoline derivative on distillation.

CUMYL-ANGELIC ACID $C_{14}H_{18}O_2$ *i.e.* $C_6H_4(C_3H_7)CH{:}CEt.CO_2H$. [123°]. From cuminic aldehyde, butyric anhydride, and sodium butyrate (Perkin, *C. J.* 31, 403). Needles (from alcohol). Forms a crystalline dibromide.

CUMYL BROMIDE *v.* BROMO-CUMENE.

CUMYL CHLORIDE *v.* CHLORO-CUMENE.

CUMYL-CROTONIC ACID $C_{13}H_{16}O_2$ *i.e.* $C_6H_4(C_3H_7).CH{:}CMe.CO_2H$. [91°]. From cuminic aldehyde, propionic anhydride, and NaOAc (Perkin, *C. J.* 31, 403; 35, 137). Nodules (from alcohol) or prisms (from light petroleum).—AgA': bulky pp.

Di-bromide $C_6H_4(C_3H_7)CHBr.CMeBr.CO_2H$. [110° 150°]. Prisms. Converted by KOH into allyl-isopropyl-benzene.

ψ-CUMYLENE-*m*-DIAMINE $C_6HMe_3(NH_2)_2$ [1:3:4:2:6]. [84°]. Formed by reduction of nitro-ψ-cumidine (from tri-nitro-ψ-cumene) or of the corresponding nitro-ψ-cumidine sulphonic acid. Long thick needles. Fe_2Cl_6 gives a dark red colouration. Gives the Bismarck-brown and chrysoidine reactions. The hydrochloride forms white plates (Mayer, *B.* 20, 970).

Isomerides *v.* DI-AMIDO-CUMENE.

CUMYLENE BROMIDE *v.* DI-BROMO-CUMENE.

DI-ψ-CUMYL-ETHYLENE-DI-KETONE [5:4:2:1]. $C_6H_2Me_3.CO.CH_2.CH_2.CO.C_6H_2Me_3$ [1:2:4:5]. [120°]. Formed by the action of succinyl-chloride upon ψ-cumene (over 2 mols.) in presence of Al_2Cl_6. On oxidation it gives tri-methyl-benzoic acid [150°] (Claus, *B.* 20, 1378).

ψ-CUMYL-ETHYL-KETONE-ω-CARBOXYLIC ACID $C_6H_2Me_3.CO.CH_2.CH_2.CO_2H$ [5:4:2:1]. [105° uncor.]. Its chloride is formed by the action of succinyl chloride (1 mol.) upon ψ-cumene (1 mol.) in presence of Al_2Cl_6. Small colourless crystals (Claus, *B.* 20, 1378).

ψ-CUMYL-HYDRAZINE $C_6H_2(CH_3)_3.NH.NH_2$ [1:3:4:6]. [120°]. Formed by reduction of the sulphite of diazo-pseudo-cumene with zinc-dust and acetic acid, and heating the sulphite which is formed with dilute HCl (Haller, *B.* 18, 91). Colourless needles, v. sol. alcohol and ether, nearly insol. water. By boiling with aqueous $CuSO_4$ it is converted into pseudo-cumene.

CUMYLIDENE-ETHYLENE-ANILINE *v.* DI-PHENYL-ψ-CUMYL-METAPYRAZOL-TETRA-HYDRIDE.

CUMYLIZIN-ACETO-ACETIC ETHER *v.* ACETO-ACETIC-ETHER-CUMYL-HYDRAZIDE.

DI-CUMYL DI-KETONE is *Cuminil* *v.* CUMINIC ALDEHYDE.

CUMYL PROPYL-BENZYL KETONE is *Deoxy-cuminoin* *v.* CUMINIC ALDEHYDE.

ψ-CUMYL MERCAPTAN $C_9H_{12}S$ *i.e.* $C_6H_2Me_3(SH)$ [1:2.4:5]. [87°]. (235°). Formed by reduction of ψ-cumene sulphonic chloride (Beilstein a. Kögler, *A.* 137, 322). Laminæ (from alcohol).—$(C_6H_2Me_3S)_2Hg$: needles (from alcohol) (Radloff, *B.* 11, 32).

CUMYL METHYL KETONE $C_6H_4Pr.CO.CH_3$. (253° i.V.). S.G. $\frac{15}{15}$ ·976. From cumene, AcCl, and Al_2Cl_6 (Widmann, *B.* 21, 2225).

Oxim $C_6H_4Pr\,C(NOH).CH_3$. [71°]. Trimetric tables (from ligroin)

p-**CUMYL-PROPIONIC ACID** $C_{12}H_{16}O_2$ *i.e.* $C_6H_4(C_3H_7).CH_2\,CH_2.CO_2H$. [76°]. From cumyl-acrylic acid and sodium-amalgam or HI (Perkin, *C. J.* 31, 388; Widmann, *B.* 19, 2773). Laminæ (from ligroin). AgA′.

ψ-CUMYL DISULPHIDE $(C_6H_2Me_3)_2S_2$. [115°]. From ψ-cumyl mercaptan and ψ cumene sulphonic acid in alcohol (Radloff, *B.* 11, 32).

DI-ψ-CUMYL-THIO-UREA $SC(NH.C_6H_2Me_3)_2$. [146°]. Formed by heating ψ-cumidine (221°) with CS_2. Prismatic crystals. Sol. hot alcohol, sl. sol. ether, insol. water (Engel, *B.* 18, 2233).

ψ-CUMYL-UREA $C_6H_2Me_3.NH.CO.NH_2$. Formed by mixing aqueous solution of (σ)-cumidine hydrochloride and potassium cyanate. White needles. Sol. hot alcohol, sl. sol. ether, insol. water. Decomposes at c. 227° without melting, evolving NH_3 and giving di-(σ)-cumyl-urea (Engel, *B.* 18, 2232).

o-**Cumyl-urea** [2:1] $C_6H_4Pr.NH.CO.NH_2$. [134°]. Small needles (Constam a. Goldschmidt, *B.* 21, 1157).

p-**Cumyl-urea** [4:1] $C_6H_4Pr.NH.CO.NH_2$. [152°]. Slender needles (C. a. G.).

Di-ψ-cumyl-urea $OC(NH.C_6H_2Me_3)_2$. [above 290°]. White silky needles. Sublimable. Sl. sol. alcohol. Formed by heating the mono-cumyl-urea, NH_3 being evolved (Engel, *B.* 18, 2233).

Di-ψ-cumyl-urea $Me_3C_6H_2.NH.CO.NH.C_6H_2Me_3$ [above 300°]. Is a product of the distillation of the ethyl or methyl ether of ψ-cumyl-amido-crotonic acid $C_6H_2Me_3.NH.CMe{:}CH.CO_2H$ (Conrad a. Limpach, *B.* 21, 528). White needles, insol. ordinary solvents.

CUPREÏNE *v.* Cinchona bases.

CUPRONINE *v.* Narcotine.

CURARINE $C_{18}H_{35}N$ (?) Occurs as sulphate in curara or urari, a resinous arrow-poison used by the South American Indians, and said to be obtained by boiling a climbing plant of the genus *Strychnos* with water. Deliquescent prisms; v. sol. water and alcohol, m. sol. chloroform, insol. ether. It is coloured red by conc. H_2SO_4. HNO_3 gives a purple-red colour. K_2SO_4 and H_2SO_4 give a violet colour like that from strychnine.—$B'_2H_2PtCl_6$: yellowish white pp. —Picrate $B'C_6H_2(NO_2)_3OH$: yellow pp. (Roulin a. Boussingault, *A. Ch.* [2] 39, 24; A. von Humboldt, *A. Ch.* [2] 39, 30; Pelletier a. Pétroz, *A. Ch.* [2] 10, 213; Pelouze a. Cl. Bernard, *C. R.* 31, 553; 40, 1327; Reynoso, *C. R.* 39, 697; Pelikan, *C. R.* 44, 507; Milleroux, *C. R.* 47, 973; Preyer, *Bl.* [2] 4, 238; Dragendorff, *Z.* [2] 3, 28; Bert, *C. C.* 1865, 958; Schnetzler, *N. Arch. ph. nat.* 24, 318; Fluckiger, *N. Repert. Pharm.* 22, 65; Koch, *C. C.* 1871, 219; Salomon, *Fr.* 10, 454; Boehm, *C. C.* 1887, 520; Sachs, *A.* 191, 254; Villiers, *J. Ph.* [5] 11, 653).

CURCUMIN $C_{14}H_{14}O_4$. [178°]. The colouring matter of turmeric root, from which it may be obtained by extracting with ether after removing an oil by ligroin (Vogel, *Schw. J.* 18, 212; Pelletier a. Vogel, *J. Ph.* 1815, 259; Vogel, jun., *A.* 44, 297; Daube, *B.* 3, 609; Schutzenberger, *Bl.* [2] 5, 194; Jackson a. Menke, *Am.* 4, 79; 6, 77; *P. Am. A.* 17, 110). Stout needles (from alcohol); nearly insol. water, benzene, CS_2, and ligroin; sol. HOAc, alcohol, and ether. Its ethereal solution exhibits green fluorescence. Its alkaline solutions are brown, but it is reppd. unaltered by acids. Salts of Ba, Ca, and Pb give brown pps. in the alkaline solution. Paper stained with curcumin and moistened with boracic acid becomes, according to Daube, orange after drying; turmeric paper becomes crimson under these conditions; in either case the colour is turned bluish-black by alkalis. Treatment with boracic acid and conc. H_2SO_4 gives 'rosocyanin,' of which the solutions are magenta and the metallic salts blue. Chromic acid mixture oxidises curcumin to terephthalic acid (Gajevsky, *B.* 6, 196). According to Kachler (*B.* 3, 713) distillation over zinc-dust yields anthracene.

Metallic derivatives $C_{14}H_{13}KO_4$: very dark crimson amorphous body, sol. water and alcohol.—$C_{14}H_{12}K_2O_4$: orange-red needles, sol. water, insol. ether. Long boiling with EtI forms a di-ethyl derivative.

Acetyl derivative $C_{14}H_{13}AcO_4$. Brown mass, sol. alcohol and HOAc, sl. sol. ether and benzene, insol. CS_2.

Diacetyl derivative $C_{14}H_{12}Ac_2O_4$. [154°]. Formed by heating curcumin with Ac_2O and NaOAc. Yellow trimetric plates. Conc. H_2SO_4 forms a blood-red solution with green reflex.

p-Bromo-benzyl derivative $C_{14}H_{13}(C_6H_3BrMe)O_4$. [78°]. From potassium curcumin and *p*-bromo-benzyl bromide in alcohol. Yellow crystals, sol. alcohol and HOAc. Oxidised by $KMnO_4$ to vanillin.

CUSCAMINE *v.* Cinchona bases.

CUSCONIDINE *v.* Cinchona bases.

CUSCONINE *v.* Cinchona bases and Aricine.

CUSPARINE $C_{19}H_{17}NO_3$. [92°]. An alkaloid present in the Angustura bark (from *Cusparia febrifuga*). An ethereal solution of this bark yields with oxalic or sulphuric acids pps. of the corresponding salts as yellow crystalline substances, which yield on decomposition the alkaloid. Long colourless needles, sol. petroleum. Decomposed by potash into an aromatic acid, and another alkaloid [250] (Korner a. Bohringer, *G.* 13, 363; *cf.* Saladin, *J. chim. med.* 1833, 9, 388; Herzog, *Ar. Ph.* [2] 93, 146).

Salts.—The sulphate, hydrochloride, and oxalate are sparingly soluble, the tartrate is readily soluble in water. The platinochloride is an orange yellow pp.

CYAMELIDE *v.* Cyanic acid.

CYAMELURIC ACID *v.* Cyanic acid.

CYAMIDO- = Cyanamido-.

CYANAMIDE *v.* Cyanic acid.

Di-cyan-diamide *v.* Cyanic acid.

CYANAMIDE-CARBOXYLIC ACID *$Cy.NH.CO_2H$. Only some salts of this dibasic acid are known (G. Meyer, *J. pr.* 126, 419). The acid, when liberated, splits up into CO_2 and cyanamide.

Salts.—$CyNNa.CO_2Na$. Formed by passing carbonic acid into a boiling alcoholic solution of sodium cyanamide: $2CyNNaH + CO_2 = CyNH_2 + CyNNa.CO_2Na$. Amorphous powder, insoluble in alcohol, soluble in water. May be obtained in groups of microscopic needles by dropping its aqueous solution into alcohol. Converted by fusion into the isomeric sodic cyanate.—$CyNK.CO_2K$. Got by passing CO_2 into boiling alcoholic potassic cyanamide. Resembles the foregoing sodium salt.—$\{CyN(CO_2)\}Ca$, 5aq. In a similar way from calcium cyanamide, by passing CO_2 into its alcoholic solution. Thin white needles, slightly soluble in water. Its aqueous solution is decomposed by heat into $CaCO_3$ and cyanamide.—$\{CyN(CO_2)\}Sr$, 2¼aq. Gritty crystalline powder, resembling the calcium salt.—$\{CyN(CO_2)\}Ba$, 1½aq. Resembles the strontium salt.

Reactions.—A solution of the potassium salt gives:—1. With silver nitrate a pp. of silver cyanamide and evolution of CO_2.—2. With basic lead acetate a white pp. of lead carbonate, cyanamide being in solution.

Ethyl ether $CN.NH.CO_2Et$. From cyanamide di carboxylic ether and alcoholic KOH (Bässler, *J. pr.* [2] 16, 146). Syrup. Readily polymerises.—$B''2HCl$: crystalline powder, v. sol. water; converted by boiling water into allophanic ether.—$CN.NNa.CO_2Et$ [241°]: needles; split up by heat into NaCyO and EtN.CO.—$CN.NK.CO_2Et$. [199°]. Converted by EtI at 150° into $CN.NEt.CO_2Et$ (213°).—$HO.Cu.NCy.CO_2Et$.—$CN.NAg.CO_2Et$.

Cyanamide di-carboxylic ether $CN.N(CO_2Et)_2$. [33°]. From sodium cyanamide and $Cl.CO_2Et$ (Bässler, *J. pr.* [2] 16, 134). Prisms. Insol. water. Boiling water decomposes it into CO_2, alcohol, and cyanamide carboxylic ether.

CYANAMIDO-BENZOIC ACID $CN.NH.C_6H_4.CO_2H$ [1:3]. [above 200°]. Flat pearly needles (containing ½ aq). Sol. hot water, alcohol and ether, nearly insol. cold water and benzene. Formed by the action of cyanogen chloride on an alcoholic solution of *m*-amido-benzoic acid.

Reactions.—Heated with baryta-water to 140° it decomposes into *m*-amido-benzoic acid CO_2, and NH_3. It is not altered by boiling with water, and only slowly with NaOH. Heated to 140° alone it evolves cyanic acid leaving a white amorphous insoluble substance. Boiled with dilute HCl it is converted into *m*-uramido-benzoic acid. With ammonium sulphide it gives *m*-thio-uramido-benzoic acid. On heating the barium-salt polymeric substances are formed. It combines with aniline to form a di-phenyl-guanidine-carboxylic acid.

Salts.—The salts of the alkalis, alkaline earths, and of Zn, Hg, Ni and Co are easily soluble. Fe_2Cl_6 gives a yellow amorphous pp. $AgNO_3$ gives a white gelatinous pp. and $CuSO_4$ gives a brown flocculent pp. (Traube, *B.* 15, 2113).

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***p*-CYANAMIDO-PHENYL-ACETIC ACID** $CN.NH.C_6H_4.CH_2.CO_2H$. [134°]. Formed by the action of cyanogen chloride on *p*-amido-phenyl-acetic acid in alcoholic solution (Traube, *B.* 15, 2121). Colourless plates or tables. V. sol. water, alcohol and ether. It is very unstable. Dilute HCl converts it into *p*-uramido-phenyl-acetic acid. $CuSO_4$ gives a brown pp. soluble in alcohol.

CYANANILINE $(C_6H_5NH_2)_2C_2N_2$.

Formation.—By the action of aniline upon oximido-ether:

$$EtO.C(NH).C(NH).OEt + 2PhNH_2 = PhNH.C(NH).C(NH).HNPh + 2HOEt$$

(Senf, *J. pr.* [2] 35, 514).

Preparation.—1. Aniline (1 pt.) is dissolved in alcohol (5 pts.) and cyanogen is passed in (Hofmann, *A.* 66, 129; 73, 180).—2. Aniline (10g.) is dissolved in alcohol (30g.) and water (60g.) is then added. On passing cyanogen gas into the solution cyananiline separates; it is purified by solution in dilute H_2SO_4 and reppn. by NH_3 (Senf, *J. pr.* [2] 35, 514).

Reactions. 1. Dry *nitrous acid gas* passed into ether containing cyananiline in suspension forms the nitrate $B''2HNO_3$. Nitrous acid gas passed into a solution of cyananiline in 65 p.c. acetic acid forms oxanilide, (1, 3, 4)-di-nitro-phenol, and phenyl-carbamine. Nitrous acid gas passed into a solution of cyananiline in glacial HOAc forms the same products, and also di-*p*-nitro-oxanilide.—2. *Sodium amalgam* forms NH_3, aniline, and formic acid. 3. *Bromine* in chloroform solution at 0° forms unstable amorphous $C_{14}H_{14}N_4Br_4$, which is probably $(C_6H_4Br.NH.C(NH).C(NH).NH.C_6H_4Br)HBr_2$ being reduced by SO_2Aq to di-bromo-cyananiline. Bromine in boiling glacial HOAc forms di-*p*-bromo-cyananiline. Bromine-water forms tri-bromo-aniline.—4. MeI at 120° gives dimethyl-aniline.—5. *Phthalic anhydride* gives phthal-anil, $C_6H_4(C_2O_2)NPh$ (Senf, *J. pr.* [2] 35, 527).

Salts.—$B''2HNO_3$: [192°]; decomposed on melting, with evolution of phenyl-carbamine.—$B''H_2Cl_2$.—$B''H_2PtCl_6$.—$B''2HAuCl_4$.—$B''H_2Br_2$.

Di-*p*-bromo-cyananiline $C_{14}H_{12}N_4Br_2$ *i.e.* $C_6H_4Br.NH.C(NH).C(NH).NH.C_6H_4Br$. [215°]. From cyananiline and bromine; or by the union of *p*-bromo-aniline and cyanogen (Senf, *J. pr.* [2] 35, 530). White plates (from alcohol).

CYANATES (METALLIC). Cyanic acid has the composition HCNO; several isomerides of this composition may exist (*v.* CYANIC ACID). The metallic cyanates are probably salts of the acid NC.OH. A polymeride of cyanic acid, $H_3C_3N_3O_3$, exists; this acid is known as *cyanuric acid.* Isomerides of this composition are possible; *cyanuric acid* very probably has the constitution $(CN)_3(OH)_3$ (*v.* p. 310), and the metallic cyanurates are salts of this acid (*v.* CYANURATES). Another polymeride of cyanic acid is also known, *Cyamelide* (*v.* CYANIC ACID).

CYANATES. Metallic cyanates are most probably all salts of the acid CN.OH. They are produced in the following among other reactions: (1) by passing cyanogen into solution of an alkali or alkaline earth; (2) by heating alkaline carbonates to low redness in cyanogen, or with mercuric cyanide; (3) by fusing alkaline cyanides or ferrocyanides with an easily reduced oxide, such as PbO_2, or with a nitrate; (4) by electrolysis of KCNAq; some cyanates are obtained from KCNOAq by double decomposition. Most metallic cyanates are soluble in water, the cyanates of Cu, Pb, Hg, and Ag are only slightly soluble. Alkali cyanates are not decomposed by heating to dull redness in dry air; in moist air they give carbonates of NH_4 and the alkali. Cyanates of the alkaline earths, and of most heavy metals, are decomposed by heat to CO_2 and cyanide of the metal (*v.* Drechsel, *J. pr.* [2] 16, 201). Acids decompose cyanates, forming CO_2 and NH_3, sometimes with a little unchanged cyanic acid; some acids ppt. solid K cyanurate from KCNOAq.

Ammonium cyanate $(NH_4)CNO$. Obtained by passing NH_3 into an ethereal solution of HCNO, or by bringing together dry NH_3 and HCNO vapour. Very soluble in water. Easily changed into its isomeride urea (Liebig a. Wohler, *P.* 20, 369, 395; *A.* 59, 291).

Potassium cyanate KCNO. S.G. 2·05. H.F. [K, C, N, O] 102,300; [KCN, O] = 72,000; [KCNO, Aq] = – 5,200 (Berthelot, *C. R.* 91, 82).

Formation.—1. By heating KCN in air, or in presence of an easily reduced oxide.—2. By passing cyanogen into KOHAq, or over heated K_2CO_3 (Wohler, *G. A.* 73, 157).—3. By electrolysing KCNAq (Kolbe, *A.* 64, 236).—4. By deflagrating KNO_3 with $K_4Fe(CN)_6$, or $Hg(CN)_2$, or nitrogenous charcoal (W., *G. A.* 73, 157).

Preparation.—4 parts dry pulverised $K_4Fe(CN)_6$ are mixed with 3 parts dry pulverised $K_2Cr_2O_7$; a little of the mixture is placed in a porcelain or iron dish, which is heated considerably below redness until the mixture becomes like tinder and blackens; the rest of the mixture is then thrown in little by little, each quantity being allowed to blacken before the next is added (complete oxidation of KCN to KCNO is thus ensured). After cooling, the contents of the dish are added to successive quantities of boiling alcohol, as much being added to each quantity of alcohol as suffices to saturate the latter; the alcoholic solution is cooled, and the crystals of KCNO are dried between paper, and then *in vacuo* over H_2SO_4. The yield is about 42 p.c. of the $K_4Fe(CN)_6$ used; if carefully conducted the KCNO contains about 1 p.c. impurities (Bell, *C. N.* 32, 99; modification of method of Liebig a. Wohler, *A.* 38, 108; 41, 289; *v.* also Clemm, *A.* 66, 382).

Properties.—Small colourless odourless laminæ, resembling $KClO_3$; fuses below redness to a colourless liquid, soluble in water, fairly soluble in boiling hydrated alcohol; insoluble in absolute alcohol.

Reactions. 1. Unchanged by *heat*; but if *water* is present the salt is decomposed to K_2CO_3 and NH_3.—2. Reduced to KCN by heating in *hydrogen*, or with *potassium*, *iron*, or *carbon*.—3. Melted with *sulphur* gives K_2S, KSCN, and K_2SO_4.—4. *Sulphuric acid* forms K_2S and KSCN with some NH_4 sulphide.—5. Heated in *hydrochloric acid gas*, KCl and NH_4Cl are formed. 6. *Sodium amalgam* reacts with a neutral solution to produce formamide $(HCO.NH_2)$.

The other cyanates have not been much studied. Insoluble cyanates, *e.g.* of Pb or Ag, may be obtained by proceeding as directed for preparation of KCNO, but exhausting the heated mass with very cold water, removing K_2CrO_4 by $Ba(NO_3)_2Aq$, and ppg by solution of a nitrate of the metal. The following cyanates have been isolated.

Barium cyanate $Ba(CNO)_2$ (Wöhler, *A.* 45, 357). By adding alcohol to a mixture of KCNOAq and Ba acetate; crystalline.

Calcium cyanate has not been crystallised; obtained by passing HCNO vapour into milk of lime.

Cobalt-potassium cyanate $Co(CNO)_2.2KCNO$ (Blomstrand, *J. pr.* [2] 3, 207). Dark blue quadratic crystals; obtained by adding KCNOAq to Co acetate solution.

Copper cyanate, not crystallised; by mixing solution of Cu acetate and Ba cyanate.

Lead cyanate $Pb(CNO)_2$ (Wöhler, *G. A.* 73, 157; Williams, *J. pr.* 104, 255). Crystalline, nearly insoluble in hot water.

Silver cyanate AgCNO (W., *G. A.* 73, 157). By adding $AgNO_3Aq$ to KCNOAq; S.G. 4·0; somewhat soluble in boiling water; dissolved and decomposed by dilute HNO_3Aq; decomposed by heating, to Ag mixed with C and some N. Soluble in NH_3Aq, giving a double compound which loses NH_3 in the air.

Sodium cyanate NaCNO. Resembles KCNO; crystalline.

Thallium cyanate TlCNO; tablets, sol. water, insol. alcohol (Kuhlmann, *A.* 126, 78).

M. M. P. M.

CYANBENZINE *v. Paranitrile* of PHENYL ACETIC ACID.

CYANBUTINE *v. Paranitrile* of VALERIC ACID.

CYANCONIINE $C_9H_{14}N_2$. (205°). S.G. ·93. Cyanethine heated with HCl gives 'oxy-cyanconiine' (*v. infra*), whence PCl_5 forms 'chloro-cyanconiine,' which is reduced to cyan-coniine. This name is given to the base by E. v. Meyer (*J. pr.* [2] 22, 286), although it is not formed in any way from coniine.

Properties.—This base dissolves somewhat in water, forming an alkaline liquid, but it separates again if the solution is warmed. It is a colourless liquid of narcotic odour. It boils at 205°. It is volatile with steam. It is poisonous, and its physiological effects resemble those due to coniine. Its aqueous solution gives with silver chloride crystalline needles of a double salt: $B'HgCl_2$, ½aq. [c. 90°].

Combinations.—1. With *ethyl iodide* at 100° forms a compound, whence by AgCl and $PtCl_4$ sharp yellow prisms of $(B'EtCl)_2PtCl_4$ may be got.—2. With *acetyl chloride* it gives unstable needles, probably B'AcCl.

Reactions.—Reduced by Zn and HCl to a new base $C_{18}H_{30}N_4$, which forms a zinc double salt (E. v. Meyer, *J. pr.* [2] 26, 340).

Oxy-cyanconiine $C_9H_{14}N_2O$. [157°]. S. ·75 at 25°. S. (alcohol of 90 p.c.) 8 at 18°.

Preparation.—1. This base is got by heating (20 g. of) cyanethine (*q. v.*) with conc. HCl (30 c.c.) for 3 hrs. at 190°. The product is evaporated, mixed with ammonia, and the pp. crystallised from water.—2. It may also be got by passing N_2O_3 into a solution of cyanethine in glacial acetic acid (v. Meyer, *J. pr.* [2] 26, 342).

Properties.—Bunches of glittering needles (from water), long striated prisms (from alcohol), or dendritic aggregates (by precipitation). May be sublimed. Sol. chloroform, benzene, and ether.

Reactions.—1. Heated with *ethyl iodide* it forms a syrup, whence by successive treatment with Ag_2O, HCl, and $PtCl_4$, trimetric crystals of $(B'EtCl)_2PtCl_4$ are formed. Hence it is a tertiary base.—2. With *acetyl chloride* forms a peculiar compound B'AcCl, not decomposed by ammonia (M.).—3. Not affected by heating with Ac_2O at 180°.—4. With PCl_5 at 140° it gives off HCl. Product shaken with solution of NaOH and extracted with ether, is found to be an oil $C_9H_{13}N_2Cl$. This reaction looks as if the base contains hydroxyl. It is converted by NH_3 at 220° into cyanethine: $C_9H_{13}N_2Cl + 2NH_3 = NH_4Cl + C_9H_{13}N_2.NH_2$. Alcoholic potash rapidly removes its chlorine forming a new base: $C_9H_{13}N_2Cl + KOEt = KCl + C_9H_{13}N_2.OEt$. The new base is an oil smelling of herbs and boiling at 230°. Its platinum salt crystallises in octahedra $(B'HCl)_2PtCl_4$. Heating with fuming HCl at 210° it is converted into the original oxy-cyanconiine: $C_9H_{13}N_2OEt + HCl = EtCl + C_9H_{14}N_2O$. These various reactions point to the presence of hydroxyl in oxy-cyanconiine and of amidogen in cyanethine. The chlorinated base $C_9H_{13}ClN_2$ may be reduced by Zn and HCl. The zinc double salt of a new base is thus got: $ZnCl_2,C_{18}H_{10}N_4 2HCl$. If this salt be treated with solution of NaOH and shaken with ether, the ether leaves, on evaporating, cyanconiine $C_9H_{14}N_2$, in the form of an oil. The base $C_{18}H_{30}N_4$, which is first formed in the reduction of chloro-cyanconiine, is readily oxidised by Ag_2O to cyanconiine.—5. With $ClCO_2Et$ oxy-cyanconiine forms a liquid carboxylic ether, which is decomposed by conc. mineral acids into the oxy-base CO_2 and alcohol (E. v. Meyer, *J. pr.* [2] 30, 121).

Salts.—Sol. water. Solutions acid to litmus.—B'HCl (at 110°).—$(B'HCl)_2PtCl_4$.—$B'HNO_3$.—$B'H_2C_2O_4$. Prisms.

Oxy-cyanconiine can occasionally act as an acid, for it forms a silver salt $C_9H_{13}AgN_2O$, sol. HNO_3 and NH_3.

Methyl derivative $C_9H_{13}MeN_2O$. [77°]. (276°). S. 8 at 18°. MeI (5 pts.) is heated with oxy-cyanconiine (2 pts.) at 150°. Crystals of $C_9H_{13}MeN_2O,HI$ are got. NaOH sets the base free. It forms white needles. Insol. potash.

Salts.—$(B'HCl)_2PtCl_4$: yellow trimetric prisms.—$HgCl_2B'$, $\frac{1}{2}$aq: needles grouped in stars.

Ethyl derivative $C_9H_{13}EtN_2O$. [43°]. (268°).

Salts.—$(B'HCl)_2PtCl_4$: tablets.—$HgCl_2B'$, $\frac{1}{2}$aq.

Ethylene derivative $C_2H_4(C_9H_{13}N_2O)_2$. [154°]. S. ·01 at 21°. From ethylene bromide (7 pts.) and the base (2 pts.) at 170°.

Salt.—$B''(HCl)_2PtCl_4$: prisms.

Constitution.—Since methyl-, ethyl-, and ethylene-oxy-cyanconiine are insol. strong potash, it would appear that the alkyls have entered an hydroxyl (E. v. Meyer, *J. pr.* [2] 26, 352). But this is not the hydroxyl corresponding to the Cl of chloro-cyanconiine, because the product of the action of KOEt upon it is a different body to the ethyl-oxy-cyanconiine here described. Nevertheless, EtI and MeI acting upon oxy-cyanconiine in presence of alcoholic potash form the above ethyl- and methyl-oxy-cyanconiines. The isomeric methoxy-cyanconiine from MeOK and chloro-cyanconiine boils at 225°. The ethoxy-base boils at 230°. E. v. Meyer thinks the isomerism can be explained thus:

ethoxy-cyanconiine $C_9H_{13}N_2(OEt)$

ethyl-oxy-cyanconiine $C_9H_{12}N(NEt)(OH)$.

CYANETHINE $C_9H_{15}N_3$. [190°]. S. ·073 at 17°. S. (alcohol of 90 p.c.) 5·8. According to E. v. Meyer (*J. pr.* [2] 35, 81) cyanethine is not the paranitrile of propionic acid $C_3N_3Et_3$, since this body, obtained by reducing α-di-chloro-propionic nitrile, has quite other properties.

Preparation.—Propionitrile (240 g.) is added gradually to sodium (30 g.), in a flask full of carbonic acid. A violent reaction occurs a few minutes after the addition of each portion. The excess of propionitrile is distilled off. The retort is broken up and the contents treated with water. The insoluble cyanethine is crystallised from 90 p.c. alcohol. The yield is 50 p.c. (Frankland a. Kolbe, *C. J.* 1, 69; E. v. Meyer, *J. pr.* [2] 22, 262). One third of the sodium becomes sodic cyanide; for every molecule of sodic cyanide formed one molecule of ethane is given off. If ether be used as a diluent, there is formed an intermediate product Me CHNa.CN, which on being treated with water yields an oil which gradually crystallises, and has the same percentage composition as cyanethine, but is polymeric with it [18°] (258°). The compound Me CHNa.CN, heated with propionitrile to 150°, yields cyanethine (E. v. Meyer, *J. pr.* [2] 37, 112).

Properties.—Monoclinic crystals (from alcohol).

Reactions.—1. With *ethyl iodide* at 160° forms B'EtI, a syrup, whence by moist Ag_2O an alkaline liquid may be got, and on adding HCl and $PtCl_4$ a well crystallised double salt $(B'EtCl)_2PtCl_4$ is obtained. But if the iodide be treated with Ag_2O, and the resulting alkaline solution be shaken with ether, the latter is found to contain ethyl-cyanethine $C_9H_{14}EtN_3$. [15°]. (260°).—2. Excess of strong *hydrochloric acid* converts it into cyanconiine $C_9H_{15}N_3 + H_2O + HCl = H_4NCl + C_9H_{14}ON_2$. It is precipitated by ammonia. 3. This same body is formed by passing N_2O_3 into a solution of cyanethine in glacial acetic acid.—4. With $ClCO_2Et$ it forms cyanethine carboxylic ether $C_9H_{13}N_2.NH(CO_2Et)$. This is a solid which melts at a low temperature and boils at (247°). It is converted by boiling alkali into cyanethine, alcohol, and CO_2. Its aqueous solution gives, with $AgNO_3$, a pp. $C_9H_{13}N_2NAg(CO_2Et)$, aq. Cyanethine carboxylic ether is decomposed by aniline with formation of an anilide $C_9H_{13}N_2.NH.CO.NHPh$ [181°]. This is a very stable body, not decomposed by hot alcoholic potash, but when heated in a current of HCl it gives off phenyl cyanate, becoming cyanethine

$C_9H_{13}N_2.NH.CO.NHPh = C_9H_{13}N_2.NH_2 + CO.NPh$ (E. v. Meyer a. Riess, *J. pr.* [2] 30, 115).—5. Combines at 100° with phenyl cyanate $C_9H_{13}N_2.NH_2 + CONPh = C_9H_{13}N_2.NH.CO.NHPh$.

Salts.—B'HCl aq.—$B'_2H_2PtCl_6$.—$B'HNO_3$: large prisms, neutral to litmus.

Combination.—B'_2AgNO_3 (at 120°): crystalline pp.

Mono-acetyl derivative $C_9H_{14}AcN_3$. [59°].

Tri-chloro-cyanethine $C_9H_{12}Cl_3N_3$. [110°] Obtained by passing Cl into a solution of cyanethine in chloroform. Resembles tri-bromo-cyanethine in its properties. N_2O_3 passed into its solution in glacial acetic acid forms tri-chloro-oxy-cyanconiine $C_9H_{10}(OH)Cl_3N_2$ [132°]. This latter may be reduced by HI to the oxy-cyanconiine.

Bromo-cyanethine $C_9H_{14}BrN_3$. [153°].

Preparation.—Cyanethine (30 g.) is dissolved in HBr and an equivalent of Br (30 g.) is added. A perbromide of hydrobromide of cyanethine separates as an oil, which soon solidifies. The whole is heated in sealed tubes at 100° for 5 hours. On cooling, crystals of the hydrobromide of bromocyanethine separate. The base is got by adding NH_3 to an aqueous solution of these crystals (C. Riess, *J. pr.* [2] 30, 146).

Properties. — Needles. Penetrating odour; v. sl. sol. water.

Salts.—$B'HNO_3$. Trimetric.—$(B'HCl)_2PtCl_4$. —$B'HClAuCl_3$ —$B'HBr$.

Reactions.—1. Boiled with alcoholic NaOEt it forms ethoxy-cyanethine (*q. v.*).—2. Fuming HCl at 200° displaces amidogen by hydroxyl, the product being $C_9H_{12}BrN_2(OH)$, [171°]. The salts of this bromo-oxy-cyanconiine are decomposed by water.—3. With *aniline* at 200° it forms $C_9H_{14}(NPhH)N_3$, phenyl-amido-cyanethine. This is insol. water, but crystallises from alcohol in plates, [125°].—4. *Zinc* and HCl reduce it to cyanethine.—5. N_2O_3 passed into its solution in glacial HOAc forms bromo-oxy-cyanconiine [172°] (E. v. Meyer, *J. pr.* [2] 26, 358).

Tri-bromo-cyanethine $C_9H_{12}Br_3N_3$. [126°]. This is formed when bromine acts on cyanethine dissolved in chloroform. It forms pearly plates insol. water, sol. alcohol, ether, and chloroform. It dissolves in strong acids, but is reppd. by water. By passing N_2O_3 into a solution of the base in glacial acetic acid, the corresponding 'tri-bromo-oxy-cyanconiine' may be formed: $C_9H_{10}(OH)Br_3N_2$, [149°].

Iodo-cyanethine $C_9H_{14}IN_3$. [152°].

Preparation.—Iodine simply combines with cyanethine, forming a per-iodide. Substitution takes place in presence of HNO_3, as follows: cyanethine (1 pt.) is dissolved in excess of dilute H_2SO_4, iodine ($1\frac{1}{2}$ pt.) is added, and then the liquid is digested on the water-bath while conc. HNO_3 is run in until all the iodine has disappeared. From the filtrate NaOH throws down iodo-cyanethine.

Properties.—Sol. acids and dilute alkalis. Decomposed by boiling NaOH.

Salt.—$B',HCl,AuCl_3$.

Reactions.—1. Iodine added to its acid solutions throws down glittering green plates of a periodide.—2. Unlike the chloro- and bromo-derivatives, it is *not* affected by passing N_2O_3 into its solution in glacial acetic acid.—3. Nevertheless fuming HNO_3, acting upon its solution in glacial acetic acid, does produce iodo-oxy-cyanconiine: $C_9H_{12}IN_2(OH)$. This may be crystallised from alcohol. It melts at [157°].—4. Dilute HNO_3 or conc. HCl (at 180°) convert iodo-cyanethine into oxy-cyanconiine, $C_9H_{13}(OH)N_2$, [156°] (Riess, *J. pr.* [2] 30, 168).

Methyl-cyanethine $C_9H_{14}MeN_3$. [74°] (c. 257°). From cyanethine and MeI at 160° (E. v. Meyer, *J. pr.* [2] 26, 343). V. sol. water, forming an alkaline solution from which it may be extracted by ether. It separates as an oil when its solution, saturated in the cold, is warmed. Cyanethine itself is very slightly soluble. Methyl-cyanethine affects the brain-cells, producing muscular contraction. Chloral, chloroform, and morphia are antidotes.

Combinations. — $B'_2,AgNO_3$. Pp. sol. hot water, separating as plates.—$B',(HCl)_2PtCl_4$.

Reaction. — 1. Heated with HCl at 180° it splits up into methylamine and oxy-cyanconiine: $C_9H_{13}N_2(NHMe) + H_2O = C_9H_{13}N_2(OH) + NH_2Me$.

Methoxy-cyanethine $C_9H_{14}(OMe)N_3$, aq. [130°]. Resembles ethoxy-cyanethine in preparation, properties, and salts. It also exchanges NH_2 for OH when acted on by N_2O_3, the product being the mono-methyl derivative of di-oxy-cyanconiine $C_9H_{12}(MeO)N_2(OH)$. This forms the salts: $B',HCl,AuCl_3$.—$C_9H_{11}Ag(MeO)N_2(OH)$ (C. Riess, *J. pr.* [2] 30, 153).

Ethoxy-cyanethine $C_9H_{14}(OEt)N_3$. [115°].

Preparation. — From sodic ethylate and bromo-cyanethine (Riess, *J. pr.* [2] 30, 148).

Properties.—Trimetric plates. Sublimes at 100°. More soluble in cold than in hot water. Its solution is alkaline to test-paper. Separated by KOH from its aqueous solution. Sol. alcohol, ether, chloroform, and acids.

Reactions.—1. An aqueous solution of the free base precipitates the hydrates of copper and lead from their salts.—2. N_2O_3 passed into a solution of the base in glacial acetic acid forms the corresponding ethyl derivative of di-oxy-cyanconiine: $C_9H_{12}(OEt)N_2OH$. This melts at [51°] and forms a silver derivative, $C_9H_{11}Ag(OEt)N_2OH$.—3. Heated with conc. HCl at 200°, it appears to form di-oxy-cyanconiine: $C_9H_{12}(OH)_2N_2$ [151°], a silver salt, $C_9H_{11}Ag(OH)_2N_2$, being analysed.

Salts.—$(B',HCl)_2PtCl_4$.—$(B',HCl)AuCl_3$.

Combinations.—$B',AgNO_3$.

CYANETHOLINE *v. supposed Ethyl ether* of *Normal* CYANIC ACID.

CYANHYDRIC ACID HCN. (*Hydrocyanic acid. Prussic acid. Formonitrile.*) Mol. w. 26·98. [−15°]. (For melting-points of mixtures of HCN and H_2O *v.* Gautier, *A. Ch.* [4] 17, 120). (26·5°). S.G. (Liquid) at 7° = ·7058, at 18° ·6969. V.D. ·966 at 40°, ·942 at 77°, ·936 at 96°, ·924 at 158°, ·903 at 198° (Gautier, *A. Ch.* [4] 17, 119). $\mu^D = 1{\cdot}263$ at 17° (Bussy a. Buignet, *A. Ch.* [4] 3, 231). μ_D for mixture of HCN and H_2O (17°) (B. a. B., *l.c.*); ratio $2HCN:H_2O = 1{\cdot}282$, $2HCN:2H_2O = 1{\cdot}297$; $2HCN:3H_2O = 1{\cdot}306$, $2HCN:4H_2O = 1{\cdot}308$. H.F. [C, N, H] = −27,480; $[C^2N^2,H^2] = 10,740$; H.C. $[CNH,O_{\frac{5}{2}}] = 158,620$ (*Th.* 2, 389). Heat of neutralisation [HCNAq, NaOHAq] = 2,770 (*Th.* 1, 295). H.V. 5,700 (Berthelot, *A. Ch.* [4] 6, 432). HCy is an extremely weak acid; the affinity is so small that the compound can scarcely be classed as an acid (*v.* Ostwald's *Lehrbuch der allgemeinen Chemie*, 2, 849). Contraction of volume occurs on mixing with water; v = vol. of HCN, v′ = vol. of H_2O, v″ = vol. of mixture; then (B. a. B., *l.c.*).

Ratio of $HCN:H_2O$	$\frac{v+v'-v''}{v+v'}$
2:1	·0328
2:1·5	·0541
2:2	·0603
2:2·5	·0611
2:3	·0623
2:3·5	·0535
2:4	·0168

Lowering of temperature occurs on mixing with water (B. a. B., *l.c.*).

Ratio of HCN:H$_2$O	Fall of temp. °
2:1	8·5
2:1·5	9
2:2	9·25
2:2·5	9·25
2:3	9·75
2:3·5	8·25
2:4	7·75

Maximum contraction and maximum fall of temperature occur when the acid and water are mixed in the ratio $2HCN:3H_2O$.

Vapour-pressure of liquid HCN at 13·25° = 472 mm. (B. a. B., *l.c.*).

Prussic acid was discovered by Scheele in 1782; it was examined by Berthollet, Proust, and others; the pure acid was prepared by Gay-Lussac in 1821 (*A. Ch.* 77, 128; 95, 136).

Occurrence.—In tobacco-smoke (Vogel a. Reischauer, *D. P. J.* 148, 231; Vohl a. Eurenberg, *A.* 147, 130). Among the products of oxidation of many carbon compounds by HNO$_3$ (Gill a. Mensel, *Z.* 1869. 65). As a product of the action of KMnO$_4$Aq on thialdine and analogous compounds, also of boiling NaOHAq on aromatic nitro-compounds (Guareschi, *B.* 12, 1699; Post a. Hübner, *B.* 5, 408). As a product of the distillation with water of parts of plants containing *amygdalin* (*q.v.* vol. i. p. 205).

Formation.—1. By subjecting cyanogen and hydrogen to the electric discharge (Boillot, *C. R.* 76, 1132); or by heating the mixture to 500°–550° (Berthelot, *Bl.* 33, 2); or by dissolving cyanogen in water and allowing to stand (Wohler, *P.* 15, 627; *v.* also CYANOGEN).—2. By the action of the induction-spark on a mixture of acetylene and nitrogen (Berthelot, *C. R.* 67, 1141; Dewar, *Pr.* 29, 188; 30, 85), or on a mixture of N with hydrocarbons which yield C$_2$H$_2$ (Berthelot, *l.c.*; Perkin, *C. N.* 21, 66).—3. By rapidly heating NH$_4$ formate or formamide with P$_2$O$_5$ (Lorin, *A.* 132, 255; Handl, *W. A. B.* 32, 252; 42, 747; Hofmann, *J. pr.* 91, 61).—4. By burning moist methylamine (Tollens, *Z.* 1866. 516). 5. By passing CHCl$_3$ vapour with NH$_3$ through a hot tube, or by heating CHCl$_3$ and alcoholic NH$_3$ to 180°–190° (Heintz, *A.* 100, 369); or by mixing CHCl$_3$ with KOHAq and NH$_3$Aq (Hofmann, *A.* 144, 116).—6. By decomposing Hg(CN)$_2$ by HClAq or H$_2$SO$_4$Aq, preferably in presence of NH$_4$Cl, and purifying by passing through CuCO$_3$ and CaCl$_2$ (Gay-Lussac; Bussy a. Buignet, *A. Ch.* [4] 3, 250).—7. By decomposing Hg(CN)$_2$ by H$_2$S, or by shaking with H$_2$SO$_4$Aq and Fe filings.—8. By decomposing AgCN by HClAq.

Preparation.—1. A cold mixture of 12 parts water with 9 parts H$_2$SO$_4$ is poured on to 8 parts coarsely powdered K$_4$Fe(CN)$_6$ in a capacious flask; the flask is connected with two bottles containing calcium chloride placed in a bath of cold water; the exit tube from the bottles passes into a dry flask surrounded by snow and salt. The mixture is warmed, and HCN passes into the CaCl$_2$-bottles; after about ½ hour the water surrounding the CaCl$_2$-bottles is warmed to 30° or so, when dry HCN passes into the flask in the freezing mixture, and is there liquefied (Pessina, *Traité de Pharmacie* de Soubeiran, 2, 337; *cf.* Wöhler, *A.* 73, 218). Great care must be taken, as HCN is frightfully poisonous; the CaCl$_2$ used should be dissolved (after use) in a large quantity of water, HCN is evolved during solution. If HCNAq is to be prepared, 10 parts K$_4$Fe(CN)$_6$ may be distilled with about 4 parts H$_2$SO$_4$ and a convenient quantity of water in a flask with very good condenser; the distillate may be rectified by distilling over MgO.—2. A solution of HCN of determined strength can be prepared by mixing KCN and tartaric acid in the ratio KCN:H$_2$.C$_4$H$_4$O$_6$ with a measured volume of water; HCNAq and KH.C$_4$H$_4$O$_6$ are formed, almost the whole of the latter is ppd. If 4 parts pure KCN are added to 9 parts tartaric acid in 60 parts water, and shaken in a stoppered bottle nearly filled by the liquid, and then allowed to stand for 12 hours, the liquid contains 3·6 p.c. HCN (Clarke, *A.* 1, 44; *cf.* Liebig, *A.* 41, 288).

Properties.—A mobile, colourless liquid, having a peculiar and very penetrating odour; does not redden litmus; *intensely poisonous*; one drop of the anhydrous acid is instantly fatal if swallowed. Inhalation of minute quantities of vapour suffices to kill, even when mixed with air the vapour is extremely poisonous; soluble in water, alcohol, and ether (for temperature and volume changes on dissolving in water, *v. ante*). Evaporation in air suffices to freeze part of the acid, crystals thus formed are transparent orthorhombic prisms. HCN or HCNAq is unstable; brown, humus-like products are formed (*v.* also *Reactions* No. 2); addition of traces of formic acid or a mineral acid serves to prevent this decomposition. Burns in air with blue flame. HCNAq is a very weak acid; its affinity is almost nothing; cyanides are generally very easily decomposed by acids.

Reactions.—1. Passed through a *tube heated to dull redness*, H, CN, C, and N are formed (Deville a. Troost, *J.* 1863. 307); *heated to about* 100° HCN forms a black mass, which at a higher temperature gives NH$_3$ and NH$_4$.CN (Girard, *C. R.* 83, 344); passed over *red hot iron* HCN is decomposed into H, C, and N (Gay-Lussac, *A. Ch.* 95, 200).—2. Even *in the cold* HCN or HCNAq easily undergoes change; brownish, humus-like bodies are formed; according to Gautier (*A. Ch.* [4] 17, 119) perfectly pure HCN does not undergo change, but if a trace of NH$_3$ is present decomposition proceeds with formation of *azulmic acid* (*q. v.* vol. i. p. 429). Traces of alkali hasten the decomposition of HCN (hence if the CaCl$_2$ used for drying contain CaO the acid produced soon begins to change), traces of acids retard the change; among the products is the polymeride H$_3$C$_3$N$_3$ (*v.* TRICYANHYDRIC ACID, p. 302). In presence of water NH$_4$ formate is produced.—3. A series of *electric sparks* passed through HCN causes partial decomposition to N and C$_2$H$_2$ with separation of a little C, after a time the C$_2$H$_2$ and N begin to recombine. An *electric current* passed through HCNAq evolves H at the negative electrode with formation of cyanide of the metal forming the positive electrode; if the HCNAq is conc. and mixed with H$_2$SO$_4$, CO$_2$ and NH$_3$ are produced (Schlagdenhauffen, *J.* 1863. 305).—4. Mixed with *oxygen*, and brought to a flame, violent explosion occurs with production of CO$_2$, H$_2$O, N, and traces of HNO$_3$.—5. *Potassium permanganate* in alkaline solution oxidises

HCNAq to HCNOAq (Péan de Saint-Gilles, *A. Ch.* [3] 55, 374).—6. *Chlorine* reacts with HCN in daylight to form $C_3N_3Cl_3$; with HCNAq it forms CNCl and HCl (Bischoff, *B.* 5, 80). According to Wurtz (*A.* 79, 280) Cl also forms $C_2N_2Cl_2$.CNH; if the HCN is in alcoholic solution a crystalline compound $C_8H_{13}ClN_2O_4$ is said to be produced (*cf.* Wurtz, *l.c.* and Bischoff, *l.c.*).—7. *Bromine* forms CNBr and HBr.—8. *Iodine* with HCNAq gives CN and HIAq.—9. *Hydrogen* (nascent) forms CH_3NH_2; the same compound is produced by passing HCN vapour and H over hot spongy Pt (Menduis, *A.* 121, 129; Linnemann, *A.* 145, 38; Debus, *A.* 128, 200).—10. *Potassium* heated with HCN gives KCN and H.—11. Reaction with *water*, *v.* beginning of this article.—12. Heated with *hydriodic acid*, NH_3 and CH_4 are produced (Berthelot, *J.* 1867. 347).—13. Conc. *mineral acids* form formic acid and NH_3; *boiling solutions of alkalis* react similarly; very conc. HClAq in the cold produces formamide (Claisen a. Matthews, *B.* 16, 308); with HCl and alcohols, alkyl salts of formic acid are produced (Volhard, *A.* 176, 135).—14. With *alkalis* in solution, alkali cyanide is formed; on heating alkali formate and NH_3 are produced.—15. Some *metallic oxides* form cyanides and H_2O, *e.g.* ZnO, HgO; others give oxy-cyanides, *e.g.* PbO, CdO; some evolve cyanogen, *e.g.* PbO_2 (Liebig, *A.* 35, 3).—16. Some *metallic salts* are decomposed by HCNAq giving cyanides, *e.g.* many acetates, some salts of Ag and Cu, some alkaline carbonates.—17. *Alkali polysulphides* form sulphocyanides.

Combinations.—1. With *water* hydrates are perhaps formed, but none has been isolated; the contraction and lowering of temperature (*v.* beginning of this art.) point to formation of $2HCN.3H_2O$; the change of M. P. on addition of water seems perhaps to indicate a hydrate $HCN.H_2O$ (Gautier, *A. Ch.* [4] 17, 120).—2. With *hydrogen peroxide* to form oxamide, $C_2O_2(NH_2)_2$ (Attfield, *C. J.* [2] 1, 94).—3. With *hydrogen* to form CH_3NH_2 (*v. Reactions*, No. 9).—4. With the *haloid acids*: HCN saturated with HCl gas at −10°, and then heated to 35°–40° forms crystals of NCH.HCl, insol. ether, sol. water, alcohol, and acetic acid; the dry compound dissociates *in vacuo* (Gautier, *C. R.* 65, 410); dry HCl passed into a mixture of HCN and $C_2H_3O.OC_2H_5$ at −10° to −15° forms white prismatic crystals of 2NCH.3HCl, insol. ether, $CHCl_3$, and acetic acid, sol. water with decomposition (Claisen a. Matthews, *B.* 16, 308). The compound 2NCH.3HBr is produced similarly to the hydrochloride (Gal, *C. R.* 61, 613; Gautier, *A. Ch.* [4] 17, 141; C. a. M., *l.c.*). When HI gas is passed into HCN the compound NCH.HI is formed, crystallises from alcohol in rhombohedra, sublimes at 300°–400° with but slight decomposition; insol. ether, sol. cold water; soon changes to HI and NH_4 formate (Gautier, *C. R.* 61, 380; Gal, *C. R.* 61, 643). 5. With *metallic chlorides*: anhydrous HCN combines with several metallic chlorides with production of much heat; the compounds are decomposed by water; the following have been obtained: (1) $TiCl_4.2NCH$ (Wöhler, *A.* 73, 226); (2) $SnCl_4.2NCH$ (Klein, *A.* 74, 85); (3) $SbCl_5.3NCH$ (Klein, *l.c.*); (4) $Fe_2Cl_6.4NCH$ (Klein, *l.c.*). BCl_3 seems to form a compound with HCN (*v.* Martius, *A.* 109, 81). 6. HCN combines directly with very many *aldehydes*, *e.g.* with acetic aldehyde it forms $C_2H_4O.NCH$ (*v.* the different *aldehydes*).

Detection and Estimation.—1. Addition of KOHAq followed by $FeSO_4Aq$ containing some ferric salt ppts. Prussian blue mixed with $Fe(OH)_2$ and $Fe(OH)_3$; addition of HCl dissolves the Fe hydroxides and leaves Prussian blue. If there be very little HCN or cyanide present, a blue-green liquid is formed, which on standing deposits bluish flocks. This test will detect $\frac{1}{780}$ grain of HCN in a very dilute liquid (Taylor, *A.* 65, 263).—2. To the liquid to be tested are added a few drops of yellow NH_4 sulphide, the liquid is evaporated on the steam-bath, $(NH_4)SCy$ is thus formed; a few drops of water are added and a drop of Fe_2Cl_6Aq, when blood-red $Fe(SCy)_3$ is formed. This test will detect $\frac{1}{3930}$ grain HCN in a very dilute liquid (Taylor, *l.c.*).—3. $AgNO_3Aq$ pps. white AgCN, e. sol. NH_3Aq, unblackened by light, sol. conc. boiling HNO_3 with evolution of CO_2. Other tests are founded on (1) the insolubility of $Cu_2(CN)_2$ in dilute HClAq (Lassaigne, *A. Ch.* 27, 200); (2) the production of a blood-red colour on heating KCNAq with picric acid (Braun, *Fr.* 1864. 464; Vogel, *C. C.* 1866. 400; (3) the blue colour produced by Cu salts with tincture of guiacum in presence of HCN (Schönbein, *Fr.* 1869. 67; Vogel, *l.c.*; Eckmann, *Fr.* 1870. 429; Link a. Mockel, *Fr.* 1878. 455). Insoluble cyanides may be fused with dry $Na_2S_2O_3$, dissolved in water, and tested with Fe_2Cl_6Aq (Frohde, *C. C.* 1863. 698). In cases of suspected poisoning, HCN is separated by distillation after acidifying the matter with tartaric acid. (For details, a manual of analysis must be consulted.)

HCN may be estimated by ppg. as AgCN, from solutions slightly acidulated by HNO_3, by addition of $AgNO_3$; haloid acids must be absent; the pp. is washed, dried at 100°, and weighed. Liebig's volumetric method may be used when haloid acids are present (*A.* 77, 102); the solution is made strongly alkaline by KOHAq, and standardised $AgNO_3Aq$ is added until a permanent turbidity is produced; the compound $AgK(CN)_2$ is produced but remains dissolved until addition of excess of silver forms insoluble AgCN. 1 c.c. of decinormal silver solution (10·8 grams Ag per litre) = ·0054 gram HCN.

Constitution. — Cyanhydric acid may be (1) HCN or (2) HNC; formula (1) represents the atom of H as directly associated with the C atom, while formula (2) represents the atoms of H and N as directly associated. The reactions of this acid with alkalis show that the H atom is acidic; the fact that the acid combines directly with the haloid acids favours the formula N.CH, which suggests the properties of a derivative of NH_3. The formation of the acid by the reaction of $CHCl_3$ with KOHAq is in keeping with the formula N.CH; this formula also suggests the production of CH_3NH_2 by the reaction of hydrogen with N.CH; the production of $H.CO_2NH_4$ when cyanhydric acid reacts with H_2O cannot decide between the formulæ N.CH and C.NH. On the whole cyanhydric acid is best regarded as the nitrile of formic acid; the formula is written N.CH.

POLYMERIDE OF CYANHYDRIC ACID. **Tricyanhydric acid.** $H_3C_3N_3$. Produced by spontaneous polymerisation of HCN, or of conc. HCNAq, in presence of alkalis, also from KCN (Lange, *B.* 6, 99; Wippermann, *B.* 7, 767; Lescœur a. Rigault, *C. R.* 89, 310). Prepared by treating the brown substance produced when HCN is allowed to change in air, with much ether, crystallising, dissolving in ether, shaking with animal char, crystallising, and re-crystallising from hot water. Triclinic crystals; v. sol. alcohol, less sol. ether. Solubility in water ·55 at 34°, 5–5·5 at 100°. Begins to decompose at 140°, melts at about 180°, and deflagrates at a higher temperature. When slowly heated with water forms HCN and the products of decomposition of this acid ($H.CO_2H$, NH_3, &c.). Heated with BaOAq, with HClAq, or HIAq, produces CO_2, NH_3, and glycocoll (Wippermann, *B.* 7, 767); hence tricyanhydric acid appears to be the nitrile of amido-malonic acid, $CN.CH(NH_2).CN$ (*cf.* Bæyer, *A.* 131, 297).

M. M. P. M.

DICYANHYDRIN *v.* Di-cyano-propyl alcohol.

CYANIC (SULPHO) ACID. SULPHOCYANIC ACID AND POLYMERIDES. (*Thiocyanic acid. Hydro-sulphocyanic acid. Sulphocyanhydric acid. Sulphocarbimide.*) Only one isomeride of the composition HCNS is known, and it is probably normal sulphocyanic acid HS.CN; the acid HN.CS has not been isolated although ethereal salts derived from it are known. A polymeride of sulphocyanic acid, viz. $H_2S_2N_2C_2$, is known, and the methylic salt of trisulphocyanic acid ($H_3C_3N_3S_4$) is also known (*cf.* Cyanic acid).

The metallic salts of the form MS.CN are described as sulphocyanides in the article Cyanides.

Preparation.—1. Dilute solutions of HS.CN are obtained by distilling excess of a sulphocyanide with dilute H_2SO_4Aq; more conc. solutions are obtained by distilling KS.CN with conc. H_3PO_4Aq, or by the reaction of H_2S with $Hg(SCN)_2$ or $Pb(SCN)_2$ (Hermes, *J. pr.* 97, 465; Zimmermann, *A.* 199, 1). 2. Sulphocyanic acid is obtained by gently heating a small quantity of $Hg(SCN)_2$ in a stream of dry H_2S (Wohler, *G. A.* 69, 271); explosions may occur if large quantities are used (Hermes, *l.c.*).

Properties.—A colourless, strongly smelling, liquid; crystallises when surrounded by snow and salt. An aqueous solution containing 12·7 p.c. of the acid has S.G. 1·04 at 17° (Hermes, *l.c.*). HSCy is a very strong acid; the affinity is nearly equal to that of HCl (*v.* Ostwald's *Lehrbuch der allgemeinen Chemie*, 2, 849).

Reactions.—1. Decomposed by *heat* to HCN and persulphocyanic acid ($H_2C_2N_2S_3$). Stable in dilute aqueous solution (about 5 p.c.); the anhydrous acid *polymerises* on standing. On distilling the aqueous acid the greater part is vapourised unchanged.—2. Heated with *mineral acids*, is decomposed to HCN and $H_2C_2N_2S_3$, or to CO_2, NH_3, and CS_2 or H_2S; the products of decomposition vary with the concentration of the solution of HS.CN used (*cf.* Völckel, *A.* 43, 74). 3. Decomposed by *sulphydric acid* (H_2S) to CS_2 and NH_3 (Völckel, *l.c.*).—4. *Oxidisers, e.g.* $KMnO_4Aq$, produce HCN and H_2SO_4 (Péan, *C.R.* 46, 626).—5. With *zinc and sulphuric acid*, reacts to form H_2S, NH_3, $NH_2(CH_3)$, and $(CH_2)_3S_3$ (Hofmann, *B.* 1. 179).—6. Heated with fairly conc. *sulphuric acid*, COS and NH_3 are produced (Than, *A. Suppl.* 5, 236).—7. *Organic acids* react to form COS and amides, or sometimes nitriles, *e.g.* $HS.CN + C_2H_3O.OH = COS + C_2H_3O.NH_2$ (Letts, *B.* 5, 669; Kekulé, *B.* 6, 113).

The metallic salts of sulphocyanic acid are described as Sulphocyanides under Cyanides. The ethereal salts of normal sulphocyanic acid, of the type Et.S.Cy, are described as Ethyl, &c., sulphocyanide; the ethereal salts derived from isosulphocyanic acid, of the type Et.N.CS, are described as Ethyl, &c., thio-carbimide.

Polymerides of sulphocyanic acid.

I. **Disulphocyanic acid** $H_2S_2C_2N_2$ (Fleischer, *A.* 179, 204). Prepared by adding alcoholic solution of KOH to persulphocyanic acid ($H_2C_2N_2S_3$; obtained by adding 3 vols. H_2SO_4Aq, S.G. 1·31, to conc. $NH_4.SCNAq$, and crystallising the crystals which separate from hot water); the crystals which separate are $K_2C_2N_2S_2$, they are collected and decomposed by dilute H_2SO_4Aq; the acid separates as a wax-like yellow mass, which hardens after a time. Sol. alcohol, nearly insol. water; when the solution is heated HSCN is formed.

II. **Trisulphocyanic acid**; this acid is not known, but its methylic salt, $Me_3S_4C_3N_3$, is obtained along with methyl thiocarbimide [Me.N.CS (*q. v.*)], by heating Me.S.Cy to 180° (Hofmann, *B.* 13, 1349).

For metallic salts of disulphocyanic acid *v.* Cyanurates and Sulphocyanurates, p. 360.

M. M. P. M.

CYANIC, DICYANIC, AND TRICYANIC ACIDS and their derivatives.—Historical Introduction.—Very soon after his inquiry into the constitution of Prussian Blue, an investigation which had enriched science with the discovery of Prussic Acid, Scheele (1786, *Opuscula* 2, 76) conducted a series of experiments with a view to determine the nature of a specimen of urinary calculus. The calculus happened to be of the acid variety. The outcome of this work was the discovery of Uric and Cyanuric or Pyro-uric acids. This is the earliest record of an oxygen compound of cyanogen. Scheele, however, did not realise that he had in his hands a hitherto unknown chemical compound. Distilling some of the calculus he obtained among other products a brown sublimate, which admitted of purification by resublimation. The properties of this sublimate are those now known to belong to cyanuric acid. Moreover, cyanuric acid may be obtained by the mode of procedure described. To Scheele the sublimate appeared to resemble succinic acid. Pearson (1798, *Tr.* 34) repeated these experiments, and observed in addition most of the characters of cyanuric acid known at the present day, but, like Scheele, this observer did not recognise the sublimate as a new substance, and was content to note its similarity to benzoic acid. Henry (1818, Thomson's *Système de Chemie*, 2, 198) was the first to point out the independent nature of the acid, and the earliest analysis was made by Chevallier and Lassaigne (1820, *A.Ch.* 13, 155).

At the same time that the cyanuric acid of Scheele was being studied, the first observations were made of three important classes of compounds—the fulminates, the cyanates, and the thiocyanates. Brugnatelli (1798, *A. Ch.* 27, 331) prepared 'Fulminating Silver,' which, however, he regarded as oxalate, and Howard (1800, *Tr.* 201) about the same time described the manufacture and properties of 'Fulminating Mercury.' That sulphur is capable of combining directly with potassium cyanide, forming 'Thiocyanate,' was first distinctly observed by Porret (1814, *Tr.* 527), the reaction having been studied previously by Buchholz (1798, *Beitrag zur Erweiterung und Berichtigung der Chemie*, 1, 88). The prediction of Gay-Lussac of a class of cyanates was verified by Vauquelin (1818, *A. Ch.* 9, 115, 22, 134), who found Ammonium Cyanate among the products of the spontaneous decomposition of cyanogen in water.

The discovery of the first compound of cyanic acid was soon followed by that of other cyanates and of the acid itself. Wohler (1822 24, *G. A.* 71, 95; 73, 157; *P.* 1, 117) analysed many of these, including the silver salt, from which he derived the formula of the acid. A little later, when heating some cyanuric acid, this chemist noticed that a gas was given off, having a peculiar pungent odour. This proved to be free Cyanic Acid, and by a suitable cooling apparatus Wöhler succeeded in liquefying it. The free cyanic acid thus obtained was examined in an important memoir by Liebig and Wohler (1830, *P.* 20, 369), and its constitution established so far as the exigencies of the time required. Liebig reverts to this question again in 1838 (*A.* 26, 122), pointing out that cyanic acid does not form double salts and is monobasic.

In the meantime a study of the fulminating mercury of Howard had furnished Liebig with some interesting results These were published in 1823 (*G. A.* 75, 393) and in conjunction with Gay-Lussac in Paris in 1824 (*A. Ch.* 25, 285). From the silver salt, which was obtained in a condition sufficiently pure, the composition, molecular weight, and basicity of fulminic acid were ascertained. The free acid was, however, not isolated. Later (1838, *A.* 26, 122) Liebig points out the relation of fulminic acid to its isomerides, cyanic and cyanuric acids. It is shown to form double salts and to be dibasic.

In the hands of Berthollet (1787, *A. Ch.* 1, 35) and Gay-Lussac (1815, *A. Ch.* 90, 200) chlorine had been made to act upon prussic acid with the formation of gaseous Cyanogen Chloride. Serullas (1828, *A. Ch.* 38, 390), now employing the same agents in the presence of sunlight, obtained a crystalline solid now known to be Cyanuric Chloride. By the prolonged action of water this compound was found to decompose, forming hydrochloric acid and a new solid, named by Serullas Cyanic Acid. This cyanic acid was perceived to be quite distinct from the cyanic acid of Wohler, but Serullas does not seem to have compared it with the pyro-uric acid of Scheele. Nevertheless, the properties noted by Serullas agree in all respects with those given by Pearson for Scheele's acid. The analysis made by Serullas, though not inaccurate for the time, entirely overlooked the hydrogen.

Wöhler made the next step forward by the discovery of a new compound, Cyanuric Acid, among the products of the action of heat on urea (1829, *P.* 15, 622). This cyanuric acid was at once compared both with the pyro-uric acid of Scheele and with the cyanic acid of Serullas. Its properties were found to agree with both of the earlier known substances, and when careful analyses were made of all three they proved to be identical. The subject is finally discussed by Liebig and Wohler (1830, *P.* 20, 369), where it is suggested that the term cyanuric acid should be adopted for the single compound whether obtained by the distillation of uric acid (Scheele), the action of water on cyanuric chloride (Serullas), or the action of heat on urea (Wohler), and that the name cyanic acid should be retained for the pungent liquid which Wöhler had found as a decomposition product of cyanuric acid, and of which Vauquelin had previously prepared the ammonium salt.

The question of the constitution of cyanic acid and its isomerides is the subject of another memoir by Liebig (1838, *A.* 26, 145). The basicity of cyanuric acid, which had been a matter of controversy between Wohler and Liebig, is finally decided by the discovery of a triargentic salt, and it is shown to have the formula $H_3C_3N_3O_32H_2O$. The analogy is pointed out between the acids of phosphorus as elucidated by Graham (1833, *Tr.* 253) and the three isomerides: --monobasic cyanic acid HCNO, dibasic fulminic acid H_22CNO, and tribasic cyanuric acid H_33CNO.

The Thiocyanic Acid, of which Porret prepared the potassium salt, was isolated by Wöhler in 1829 (*C. A.* 69, 271), and in the same year Liebig (*P.* 15, 563) came across a solid substance among the products of the action of water on cyanuric chloride which, in conjunction with Wohler, he found again (1830, *P.* 20, 386) as a product of the decomposition of cyanic acid with water. This compound isomeric with cyanuric acid, but insoluble, was called 'insoluble cyanuric acid' or, later, Cyamelide.

About this time, too, Liebig (1834, *A.* 10, 10) by acting on ammonium thiocyanate by heat produced a substance called Melam, and from this, by the action of dilute soda, a base was formed richer in the elements of ammonia. This base was regarded by Liebig as the amide of cyanuric acid, and was called from its parent substance Melamine (1834, *A.* 10, 18). Another base nearly related to these, Mellone, was obtained by the action of heat on melam, and from mellone, by treatment with nitric acid Liebig (1834, *A.* 10, 34) prepared an acid, Cyanilic Acid, which proved to be an isomeride of cyanuric acid, distinguished from the latter acid chiefly by its crystalline form and solubility.

The thirty-five years following 1840 were very largely devoted to the discovery of ethereal derivatives of cyanic and cyanuric acids, and to a study of their structure with a view to rendering intelligible the very remarkable metameric series of compounds which were brought to light. But aside from this main current of research there are many other discoveries of scarcely less importance. Two of these call for attention at once—the study of the action of heat on nitrate of urea by Pelouze (1842, *A.* 44, 106) and Wiedemann (1848, *A.* 68, 324), and the interesting reaction between cyanic acid and aldehyde whereby Liebig and Wöhler (1846, *A.* 59, 296) prepared the compound known as Trigenic Acid.

Three important series of alkyl derivatives were discovered during the years 1847-48; the cyanic and cyanuric ethers of Wurtz, and the thiocyanic ethers of Cahours. By acting on alkyl potassium sulphate with a salt of cyanic acid, Wurtz (1848, *C. R.* 26, 368; 27, 241) obtained Alkyl Cyanates, and using a cyanurate instead of a cyanate he succeeded in preparing a series of Alkyl Cyanurates. Both these classes of ethers when decomposed by water, in presence of dilute acids or alkalis, give amines and carbon dioxide, showing that they have a similar structure. The discovery of the ethers of Wurtz was partly anticipated by Cahours (1847, *A. Ch.* 18, 261), who by the analogous reaction of alkyl calcium sulphate with potassium thiocyanate obtained Alkylthiocyanates. The thiocyanic ethers do not admit of their constitution being studied by decomposition with water, but the same end is attained if they be subjected to the reducing action of nascent hydrogen. The thio-ethers of Cahours give by this treatment mercaptan and hydrocyanic acid, showing that the alkyl radicle is attached to the sulphur and not to the nitrogen.

The study of ethereal derivatives must now give way to the consideration of several new reactions which were brought to light at this time. Debus (1849, *A.* 72, 18) in his work on ethyl thiocarbamate or xanthogenamide $NH_2.CS.OEt$ or $NH_2.CO.SEt$ was led to the discovery of a reaction by which this compound breaks down into mercaptan and cyanuric acid. If the constitution of xanthogenamide were better known, an important insight might thus be obtained into that of cyanuric acid. Notwithstanding the attempts of Bineau (1839, *A. Ch.* 70, 251) to prepare an amide of cyanic acid homologous with the cyanuramide or melamine of Liebig, no such compound was isolated until Cloëz and Cannizzaro instituted their inquiry in 1851 (*C. R.* 32, 62). These chemists obtained Cyanamide by acting upon cyanogen chloride with ammonia. A very remarkable property of the cyanamide thus obtained is the ease with which it undergoes polymerisation. The result of this intramolecular rearrangement, as shown by Beilstein and Geuther (1858, *A.* 108, 99; 123, 241) is the formation of the dicyanogen homologue Dicyandiamide. An isomeric series of homologous amides is thus completed corresponding to the three classes of mono-, di-, and tri- cyanogen compounds. Employing amines instead of ammonia in the reaction of Cloëz and Cannizzaro, the alkyl cyanamides were prepared by Cahours and Cloez (1854, *C. R.* 38, 354).

Another instance of polymerisation was announced at this time by Liebig (1855, *A.* 95, 282). When fulminating mercury is allowed to stand in presence of water it gradually changes its colour and other properties. These changes were found to correspond to an entire rearrangement of the molecule, the dicyanic fulminic acid having polymerised to tricyanic Fulminuric Acid. The new acid is metameric with cyanuric acid, but in its basicity and in other respects it is quite distinct from that compound. Fulminuric acid was discovered independently by Schischkow (*A.* 97, 53; 101, 213), whose attention was also directed to the constitution of the isomeric fulminic acid from which it is derived. Mercuric fulminate, according to Schischkow (*J. R.* 16, 276), is $Hg(CN)_2.C_2(NO_2)_2.Hg$, and fulminic acid $(HCN)_2.C_2H_22NO_2$. On the other hand Kekulé (*A.* 101, 200; 105, 279), in view of other reactions, regarded fulminic acid as nitro-acetonitril CH_2NO_2CN.

Returning once more to the ethers, a reaction must be noticed that was first studied by Cloëz (1857, *C. R.* 44, 482), which in the hands of Hofmann and other later investigators has done much to give order to the knowledge of cyanic derivatives. Cloez caused cyanogen chloride to act on sodium ethylate, and obtained a compound which he called Cyanetholine and which has sometimes been regarded as consisting of a cyanic ether isomeric with that of Wurtz. Gal (1866, *C. R.* 61, 527), who observed its decomposition products, correctly so regarded it, and moreover judged that it was related to the cyanic ethers of Wurtz in the same manner that the nitriles are related to the isonitriles.

Still another reaction was announced at this time for the preparation of ethers. Habich u. Limpricht (1859, *A.* 109, 111) discovered that silver cyanurate and alkyl iodides react, forming cyanuric ethers identical with those of Wurtz.

The Cloez reaction was now, in 1870, the subject of an important investigation by Hofmann and Olshausen (*B.* 3, 269). No cyanic ether was found, but, instead, these observers succeeded in preparing a series of Cyanuric Ethers metameric with those of Wurtz. The methyl analogue of the cyanetholine of Cloez and Gal proves to be a mixture containing cyanuric ether and an amido-derivative. Cyanic ethers homologous with these cyanuric ethers and metameric with the cyanic ethers of Wurtz have never been isolated. Hofmann and Olshausen were led to predict the formation of a series of cyanuric ethers in this reaction from its analogy to that of Cloez and Cannizzaro for cyanamide and Cahours and Cloez for alkyl cyanamides, thus:—

$$\mathrm{Cl}|\boxed{\mathrm{CN+(NH)H}}|\mathrm{H} \text{ (Cloez and Cannizzaro)}$$

$$\mathrm{Cl}|\boxed{\mathrm{CN+(NH)Et}}|\mathrm{H} \text{ (Cahours and Cloez)}$$

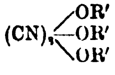
$$\mathrm{Cl}|\boxed{\mathrm{CN+OEt}}|\mathrm{H} \text{ (Hofmann and Olshausen).}$$

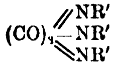
Now in the second reaction the alkyl cyanamide was known to polymerise readily at the moment of its formation to alkyl melamine. Just in the same manner, thought Hofmann and Olshausen, might the product of the third reaction, which differs only in containing oxygen for imidogen, polymerise at the moment of its formation to a cyanuric ether. This hypothesis was confirmed by experiment.

The cyanuric ethers thus obtained when submitted to the action of water in presence of dilute acids or alkalis give cyanuric acid and alcohol, showing that the alkyl radicle is attached to the oxygen and not to the nitrogen, as it would seem to be in the case of the Wurtz ethers. It would thus appear that the Wurtz ethers are substituted imide compounds, while those of Hofmann and Olshausen are substituted hydroxyl derivatives. The reaction of both with water then becomes clear, thus:—

Hofmann and Olshausen.	Wurtz.
$C_3N_3\,3OR'$	$C_3O_3N_3R'_3$
$O_3H_3H_3$	O_3H_6
$(CN)_3 3OH \vert 3R'OH$	$3CO_2 \vert 3NH_2R'$

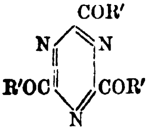
The difference between these two classes of ethers may be represented by the formulæ:—



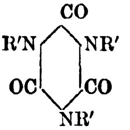


or better still by the use of ring formulæ, a device which is especially useful when more complex reactions have to be studied. The ether corresponding to the hydroxyl acid is of course the normal or ortho-ether, while the imide substituted ether is the iso-ether:—

Normal ether of Hofmann and Olshausen.



Iso-ether of Wurtz.



In the same manner the normal cyanic ether which in the Cloez reaction is probably formed in the first instance, but which has not been isolated, may be supposed to be related to the cyanic ether of Wurtz:—

$$(CN).OR'$$

Hypothetical normal cyanic ether.

$$(CO):NR'$$

Isocyanic ether of Wurtz.

And the decomposition by water of the two ethers may be represented:—

$$\begin{array}{c} CNOR' \\ HOH \\ \hline (CN)OH \mid R'OH \end{array}$$

Decomposition of hypothetical normal ether.

$$\begin{array}{c} CONR' \\ OH_2 \\ \hline CO_2 \mid NH_2R' \end{array}$$

Decomposition of iso-ether.

A very interesting instance of intramolecular change was announced by Hofmann and Olshausen in this same memoir. It was noticed that the melting-point of trimethyl normal cyanurate changed on continued heating. In the first place it melts at 132°, but after heating for some time the melting-point rises and remains constant at 175°. Metastasis was suspected, and it was found that, while before the application of heat the cyanurate gave when decomposed with water alcohol and cyanuric acid, after that operation its decomposition products were carbon dioxide and amine. The normal ether had changed into the corresponding iso-ether of Wurtz. Such instances of intramolecular migration from normal to iso- in the case of alkyl derivatives of cyanogen compounds are now known to be of frequent occurrence.

Of the thio-analogues of these isomeric ethers, one series had been discovered by Cahours. On reduction with nascent hydrogen they gave mercaptan and hydrocyanic acid. These were the analogues of the hypothetical normal cyanic ethers. The series of isomeric thiocyanates corresponding to the cyanic ethers of Wurtz were synthesised by Hofmann (1868, *B.* 1, 25 a. 169; 2, 452; 7, 814; 8, 106), and constitute the 'mustard oils' of which ordinary mustard oil is a member. When the mercury salt of monoalkyldithiocarbamic acid is distilled it loses mercuric sulphide, and sulphuretted hydrogen and alkyl thio-isocyanate passes over. The thio-isocyanic ethers give on treatment with nascent hydrogen not mercaptan and hydrocyanic acid but amines and thio-aldehyde. The two reactions may be seen thus:—

Normal thio-ether of Cahours.

$$\begin{array}{c} CN.SR' \\ H \quad H \\ \hline CNH \mid R'SH \end{array}$$

Isothio-ether of Hofmann.

$$\begin{array}{c} CS:NR' \\ H_2 \quad H_2 \\ \hline HCHS \mid NH_2R' \end{array}$$

The following discoveries also belong to this period:—The production of isocyanic ethers from isonitriles by direct oxidation accomplished by Gautier (1869, *C. R.* 67, 804). The discovery of Dicyanic Ethers and Alkyl Melamines by Hofmann (1861, *A. Suppl.* 1, 51; *B.* 3, 765; 1869, *B.* 2, 602; 3, 264). The former by polymerisation of phenyl-isocyanate in presence of triethylphosphine, and the latter by desulphurisation of monoalkylthio-urea in which case alkyl cyanamide is doubtless first formed and then changed into the polymeric melamine. Finally, the experiment of Beilstein (1860, *A.* 116, 357), which showed that cyanuric acid treated with phosphorus pentachloride gives cyanuric chloride. Cyanuric chloride is thus seen to be related to cyanuric acid precisely in the same way as acetyl chloride for example is related to acetic acid. It may be obtained from the acid by substitution of its hydroxyl by chlorine when treated with phosphorus pentachloride, and, as Serullas was the first to show, the chloride by treatment with water loses its chlorine and again assumes hydroxyl in its place, becoming cyanuric acid.

A period is now reached, commencing about the year 1875 and extending to the present day, during which the activity of investigators in this subject has been directed in the main to the question of the constitution of cyanic and cyanuric acids. To these must be added melamine, for just as the acids give rise each to two parallel series of metameric ethers, so, as it will appear, does melamine. This isomerism has not yet been found among the alkyl cyanamides or dicyanic diamides. It will be seen that in the case of the parent hydrogen compounds no reactions have been discovered which permit, as in the case of their alkyl derivatives, the assertion that the one is normal or of the hydroxyl type, and the other iso- or of the imide type.

The discussion was inaugurated by Nencki (1876, *B.* 9, 232), who, working on the compound aceto-guanidine, found that by a series of reactions it is converted finally into cyanuric acid. In a second communication (*B.* 9, 244) he suggested an explanation of these reactions assuming the imide nature of cyanic acid. This procedure led of course to the view that cyanuric acid is iso- or imide in its constitution. Further evidence in favour of the imide structure of both cyanic and cyanuric acids is found according to Fleischer (*B.* 9, 436) in the desulphurisation of ammonium thiocarbamate $NH_2.CO.SNH_4$ by which reaction either urea or iso-cyanate should result: experiment showed that ordinary ammonium cyanate was formed. Weith (*B.* 9, 454) then joined the controversy, and proposed an altogether new set of formulæ for the compounds obtained by Nencki from aceto-guanidine. Nevertheless, while pointing out that the imide nature of the acids was not proven, he considered the weight of evidence to be in favour of that view. Michler (*B.* 9, 715) advanced another reaction to support the iso-theory, the distillation of *u*-diphenylurea, which yields cyanic acid and diphenylamine. This reaction has, however, no more value as proof than the action of heat on urea itself.

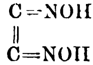
So far the evidence had been very largely in favour of the iso-hypothesis. Claus (*B.* 9, 721) now joined issue with the preceding observers. He questioned the value of the little understood guanidine reactions of Nencki as proof of constitution, and showed, as Weith had indeed already done, that with equally probable assumptions the changes observed by Nencki might be explained so as to support the opposite view. Similarly he contended against Fleischer that the formula for ammonium thiocarbamate is by no means established, and if the alternative hydroxyl formula, $NH_2.CS.ONH_4$, be used, the reaction supports the normal hypothesis. To these criticisms both Nencki and Fleischer replied, Fleischer (*B.* 9, 988) defending the formula which he had employed for thiocarbamic acid, and Nencki (*B.* 9, 1008) considering at length the evidence for and against the two contending theories. The leading points are as follows: *For the imide or iso- formula.*—1. The easy breaking down of cyanic acid by the action of water into ammonia and carbon dioxide $CONH + OH_2 = CO_2 + NH_3$.—2. The conversion of cyanic acid into formamide by the action of nascent hydrogen $CO{:}NH + H_2 = H.CO.NH_2$.—3. The reaction of Wurtz in which cyanates and cyanurates yield iso- and not normal ethers $(CON)K + KR'SO_4 = CONR' + K_2SO_4$. *For the hydroxyl or normal formula.*—1. If in order to explain all the reactions of these bodies it is found necessary to assume an intra-molecular change, it is easier to imagine it taking place from the normal to the iso- than from the iso- to the normal atomic arrangements, since it is known with what ease normal cyanic and cyanuric derivatives change to the iso- condition, and thus to suppose that in the Wurtz reaction normal ether is at first formed and that it immediately changes to iso-ether.—2. Finally, Beilstein had shown that cyanuric chloride, the normal structure of which does not admit of question, is the chloride corresponding to cyanuric acid. Nencki admits that the acetoguanidine reactions tell equally for both theories. Nencki concludes, however, with Weith that the weight of evidence is in favour of the imide structure. The discussion was continued by Claus (*B.* 9, 1165), Fleischer (*B.* 9, 1459), and Nencki (*B.* 9, 1552), but little further advance was made.

The fundamental distinction between mono-, di-, and tri-cyanic acids which Liebig so clearly pointed out has been confirmed, and its value appreciated more and more. It may be that fulminic acid is not the dicyanic acid homologous with cyanic and cyanuric acids, and that this has yet to be discovered. Indeed, there may be many such mono-, di-, and tri-cyanogen series to which the numerous isomerides of cyanic acid of which the constitution is at present so little known will contribute members.

By the help of this conception a place is ready for the Thiodicyanic Acid discovered in 1876 by Fleischer (*A.* 179, 204), and perhaps for several new isomerides of cyanic acid which have now to be noticed. It was just at this time that Herzig (*B.* 12, 170) announced the discovery of *α*- and *β*-Cyanuric Acids. These new acids were said to be obtained by the action of hexabromacetone on urea. It has, however, recently been shown (Senier, *C. J.* 49, 693; 49, 743) that both these acids are merely ordinary cyanuric acid disguised by traces of impurities. The isomerism of the cyanamido-carbonic acid discovered by J. Meyer (1878, *J. pr.* 18, 419) is merely coincidental, that compound having nothing further in common with cyanuric derivatives. Four isomerides, however, remain to be noted, all derived from fulminic acid. The first is Isofulminuric Acid. It was prepared by Ehrenberg (1884, *J. pr.* 30, 38) by acting on an ethereal solution of free fulminic acid with ammonia. The remaining three isomerides were discovered by Scholvien (1885, *J. pr.* 32, 461), and all arise out of the action of dilute sulphuric acid on fulminates. They are Meta-fulminuric Acid, *β*-Isofulminuric Acid, and Iso-cyanilic Acid. Metallic salts of each were described, but no alkyl or other derivatives.

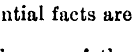
In the present state of their history it would be premature to speculate as to the constitution of this remarkable group of isomerides. It may, however, be worth while to bear in mind that the possible metamerides of cyanuric acid are very great, especially when mixed types are considered, as, for instance, the two conceivable intermediate acids between normal and iso-cyanuric acid (*cf.* Senier, *Inaug. Dissert.*, Berlin, [1887] 28).

A further study of these fulminuric acids may help to clear up the constitution of fulminic acid itself, for like the latter acid some of them evolve hydroxylamine when decomposed by water in presence of hydrochloric acid. It was on this account that Steiner (1883, *B.* 16, 1484) suggested the following isonitroso-formula for fulminic acid



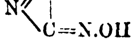
$$\begin{array}{l} C{=}NOH \\ \| \\ C{=}NOH \end{array}$$

, whereas he had previously (1876, *B.* 9, 782) been an adherent of Kekulé (1857, *A.* 101, 200; 105, 279), who regarded it as nitroacetonitrile. The recent work of Divers ([1885] *C. J.* 47, 79) has led to another formula



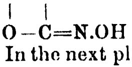
$$O\left\langle\begin{array}{l} N{=}CH \\ \quad\;\; | \\ N{=}COH \end{array}\right.$$

. According to Armstrong, the essential facts are best represented for the present by one of the following,



$$N\left\langle\begin{array}{l} C{-}OH \\ | \\ C{=}N.OH \end{array}\right.$$

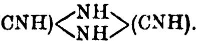
or



$$\begin{array}{l} N{=}CH \\ |\quad\;\; | \\ O{-}C{=}N.OH \end{array}$$

(*C. J.* 47, 79).

In the next place two announcements call for notice which have an interesting bearing on the constitution of cyanuric acid. The first is the production of melanurenic acid, a derivative of cyanuric acid, by Bamberger, by the action of water on dicyandiamide (*Inaug. Dissert.*, Berlin 1880; *B* 16, 1074; 16, 1459; 16, 1703). Bamberger ascribes to dicyandiamide the formula $C{:}NH.NH_2{:}NHCN$ as preferable to Baumann's formula (1873, *B.* 6, 1375),



$$(CNH)\left\langle\begin{array}{c} NH \\ NH \end{array}\right\rangle(CNH)$$

. The second is the study of the absorption spectrum of cyanuric acid which led Hartley (1882, *C. J.* 41, 48) to the conclusion that it has a ring formula and doubly-linked atoms. This is of course quite in accord with the normal or hydroxyl theory.

There remain to be considered the important researches of Hofmann, Klason, Ponomareff, Mulder, and Rathke. These investigations are for the most part contemporaneous. They also largely supplement one another; and although they do not explicitly support the same hypothesis, they do not take the form of a discussion. Only an outline of the more important features of this work can be attempted here.

Commencing with Mulder in the year 1882: the Cloez reaction was the first to engage the attention of this observer (*R.* 1, 41, 191; 2, 133; 3, 287). The results in the ethyl series were similar and parallel to those in the methyl series of Hofmann and Olshausen. The most interesting observation is that normal cyanic and cyanuric ethers give bromine addition compounds, while the isocyanic and cyanuric ethers form no such combinations. This, according to Mulder, becomes a test by which the one structure can be distinguished from the other. Now cyanuric acid does not combine with bromine, and hence it is regarded as iso- in constitution. The compound with cyanuric ethyl ether has the formula $C_3N_3O_3Et_3Br_6$. By the use of this test Mulder was led in 1885 to recognise the diethyl cyanuric ether of Habich and Limpricht as an iso- compound (*R.* 4, 91). Subsequent observation has, however, not confirmed the value of this reaction as a test in all cases.

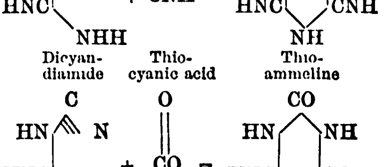
Many attempts have been made to discover among the metallic cyanates and cyanurates isomeric differences like those found among the ethers. An investigation of Calmels in 1884 (*C. R.* 99, 239) would seem to show that metallic cyanides analogous to the nitriles and carbamines exist, but hitherto no one has found evidence of a similar isomerism among the metallic cyanates or cyanurates. The experiments of Mulder in 1882 (*R.* 15, 69) with this object proved as fruitless as those of Bannow (1871, *B.* 4, 254; 13, 2201) had been.

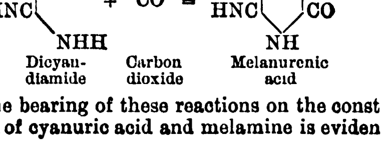
Mulder suggested new formulæ for bromide and chloride of cyanogen N_3,3CBr and N_3,3CCl, and in a series of communications in 1885-6 (*R.* 4, 47; 4, 151; 5, 65; 5, 84; 5, 99) studied the properties of the bromide. The curious fact was noted that pure cyanogen bromide does not polymerise, but that this change takes place readily in presence of a trace of free bromine. Two curious addition products of cyanogen bromide with ethyl cyanurate are described $C_3N_3O_3Et_3$,2BrCN and $C_3N_3O_3Et_3$,BrCN (*cf.* Senier, *Inaug. Dissert.*, Berlin, 1887, 34).

As in the case of Mulder, so the work of Ponomareff commenced with a study of the cyanetholine of Cloez. This chemist in 1882 (*B.* 15, 513) arrived at results in accordance with those of Hofmann and Olshausen, and proposed the use of mercuric chloride to distinguish iso- from normal cyanuric compounds. This reagent gives crystalline addition compounds with normal derivatives, that in the case of normal ethyl cyanurate being $(CN)_3 3OEt,HgCl_2$. Unfortunately, like the corresponding bromine test of Mulder, this mercuric chloride test has been shown to be inapplicable to all cases (Hofmann, 1885-6, *B.* 18, 2796; 19, 2093).

The study of the formation of cyanuric ethers and the preparation of alkoyl derivatives in the hands of Ponomareff threw additional light on their structure. Hofmann and Olshausen had prepared the cyanuric ethers by the Cloez reaction, using cyanogen chloride. The method was simplified by Ponomareff in 1885 (*B.* 18, 3261), who employed the already polymerised cyanuric chloride. By this means he obtained normal cyanuric ethers which gave cyanuric chloride again when treated with phosphorus pentachloride, and gave melamine by the action of ammonia. In the next place this observer studied the reaction of Habich and Limpricht, by which only isocyanuric ethers had been obtained. By allowing the alkyl iodide to act on silver cyanurate at a low temperature there was always formed together with the isocyanurate some ether that gave a crystalline compound with mercuric chloride, and hence was judged by Ponomareff to be normal ether. The experiment was afterwards repeated by Hofmann and the crystalline mercuric chloride compound examined (1886, *B.* 19, 2093), but it was proved that the mercuric chloride was combined not with normal but with iso- ether. In the same memoir Ponomareff described the first alkoyl derivative of cyanuric acid, triacetyl cyanurate. The corresponding tribenzoyl cyanurate was obtained soon afterwards by Senier (1886, *C. J.* 49, 313).

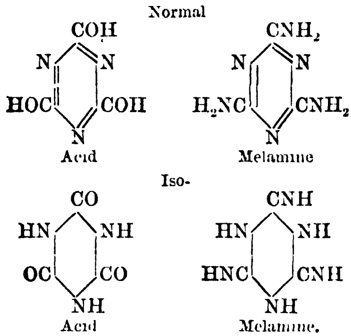
The reaction between dicyandiamide and carbon dioxide already pointed out as giving rise to a mixed cyanuric acid and melamine, melanurenic acid, was made the basis of an interesting communication from Rathke in 1885 (*B.* 18, 3102). This inquirer noted that when such compounds as H_2O or NH_3 or CO_2, which can divide into two divalent radicles, for instance $H_2 + O$, $H_2 + NH$, and $O + CO$, combine to form addition compounds with cyanogen derivatives, they do so in accordance with a general law, the one residue joining the carbon and the other the nitrogen. Thus nitriles take up the residues of water or sulphuretted hydrogen, giving acid amides or thio-amides, or they take up ammonia or amines forming amidines. To this class of reactions belongs, according to Rathke, the conversion of dicyandiamide into melanurenic acid, and also the parallel reaction announced for the first time between dicyandiamide and thiocyanic acid, where combination to thioammeline takes place. Using Bamberger's formula for dicyandiamide, the reactions may be represented thus:—





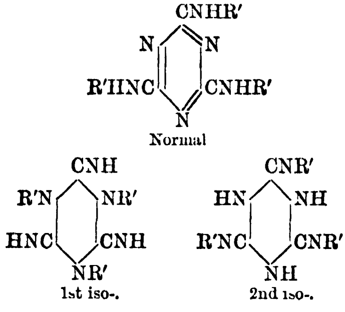
The bearing of these reactions on the constitution of cyanuric acid and melamine is evident.

Ammeline and melanurenic acids are amido-acids between melamine and cyanuric acid, and if the above expressions be the true ones, both the acid and melamine are imido- or iso- and not normal compounds. The following formulæ showing cyanuric acid and melamine both as normal and iso- compounds will assist in making this clear:—



According to Hofmann the weight of evidence is in favour of the view that both these compounds are normal in constitution. Rathke pointed out that these two reactions must be considered, and whether the formula of Bamberger be employed or the alternative one of Baumann, they both lead to the conclusion that thio-ammeline and melanurenic acid are iso-compounds, and indirectly to the iso- nature of cyanuric acid and melamine. One class of reactions requires the one formula, another class of reactions the other. In Rathke's view it is impossible to find a formula to account for both classes of reactions. It seems that the position of the hydrogen atoms, unlike that of the alkyl radicles, is not stable, and that indeed both formulæ may be employed side by side. In the same manner Rathke recommends the use of two formulæ for hydrocyanic acid, acetacetic ether, the lactam and lactim groups, thio-urea, and other similar cases.

In another communication (1887, *B.* 20, 1056) this standpoint was developed further, and in view of the discovery of several triphenylmelamines Rathke suggested the addition of a third imide type for alkyl melamines, thus:—



The radicles attached directly to the ring as in the first iso- form are said to be in the *eso*- position, while those attached to side chains as in the second iso- form are termed *exo*-. This system was suggested in order to account for the instances of complex isomerism in the case of phenylmelamines, which Hofmann was the first to point out. In the communications following, Rathke ([1887-8], *B.* 20, 1065; 21, 867; 21, 874) announced several new complex derivatives, the constitution of which he studied by means of this hypothesis. These are Phenyl Thiammeline, Triphenyl Ammeline, Monophenyl Iso-cyanuric acid, Diphenyl Melamine, and Triphenyl Melamine.

No inquirer in this department of chemical research has been more unwearied, and none has been more successful, than Hofmann. As early as 1857, in conjunction with Cahours (*A.* 102, 293), he discovered allyl cyanate, and from that time to this he has reverted to the subject again and again. The earlier communications have been already noticed, but there remain a series of exhaustive critical memoirs which have appeared during the last few years of which only the barest outline can be given. They are an attempt to settle the question of the constitution chiefly of cyanuric acid and melamine, but they bring into their service numerous new reactions and classes of compounds.

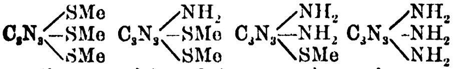
In one of the first of these, in 1881 (*B.* 14, 2728), Hofmann described a new reaction in which iso-ethers are among the products. It is the action of heat on alkyl acetyl urea. Together with isocyanic ether di- and tri-alkyl isocyanurate are formed. In another paper in 1880 (*B.* 13, 1349) some interesting instances of intramolecular change are described. Just as the cyanic methyl ether at first formed in the Cloez reaction was found by Hofmann and Olshausen to polymerise to methyl cyanurate, so the same change is now effected in the case of methyl thiocyanate, which is converted into methyl thiocyanurate, and also (1885, *B.* 18, 765) in that of phenyl isocyanate, which becomes phenyl isocyanurate. The general tendency of the normal to pass over into the more stable iso- atomic arrangement finds another example here, for together with the trimethyl-thiocyanurate some of the iso- compound is always formed. Hofmann called attention to the fact that pure methyl-thiocyanate does not polymerise by heat alone, but does so in presence of a little hydrochloric acid. It will be remembered that in the same manner Mulder found that cyanogen bromide only admitted of polymerisation when mixed with some other substance, as, for instance, with free bromine. The action of such agents as hydrochloric acid and free bromine in these instances, and the still more remarkable action of triethylphosphine or pyridine (Snape, 1886, *C. J.* 49, 254), which convert phenyl isocyanate only into dicyanate, while if certain dry salts are substituted, sodium acetate, sodium formate, or sodium carbonate, the intramolecular re-arrangement goes as far as the production of cyanurate; these are facts of which chemistry in its present state of development offers no explanation.

From methyl-thiocyanurate thus obtained Hofmann isolated in 1885 for the first time free Thiocyanuric Acid (*B.* 18, 2196). The methyl ether, by treatment with sodium sulphide, is converted into the sodium salt, methyl mercaptan being formed at the same time, and the sodium salt, when treated with hydrochloric acid, has its sodium replaced in three stages, forming two intermediate acid sodium thio-cyanurates, and finally free thio-cyanuric acid. The sodium salt of thiocyanuric acid may be also prepared from cyanuric chloride by the action of sodium mercaptide.

Pursuing the inquiry still further into the behaviour of this thio- analogue of cyanuric acid, the action of ammonia and amines on the trimethyl ether was investigated in 1885 (*B.* 18, 2755). Water decomposes the ether in accordance with the general reaction into cyanuric acid and mercaptan, and it was thought that ammonia might similarly give mercaptan and melamine, thus:—

$$(CN)_3 3SMe + 3H(HO) = (CN)_3 3OH + 3MeSH$$
$$(CN)_3 3SMe + 3H(NH_2) = (CN)_3 3NH_2 + 3MeSH\text{·}$$

Experiment proved this to be the case. Melamine is thus advantageously prepared. The reaction takes place, however, in three stages, two intermediate compounds being formed—mono-amido- and di-amido- ether—thus:—

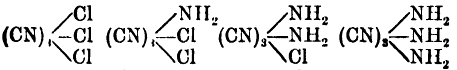


$$C_3N_3\begin{cases}SMe\\SMe\\SMe\end{cases}\quad C_3N_3\begin{cases}NH_2\\SMe\\SMe\end{cases}\quad C_3N_3\begin{cases}NH_2\\NH_2\\SMe\end{cases}\quad C_3N_3\begin{cases}NH_2\\NH_2\\NH_2\end{cases}$$

ether intermediate compounds melamine.

The action of substituted ammonias was now tried, and corresponding alkyl melamines and intermediate alkyl amido- ethers resulted.

Melamine and alkyl melamines are also produced, as was expected, from cyanuric chloride, and ammonia or amines, and in this case, too, a series of intermediate amido- and alkyl amido- cyanuric chlorides was obtained, thus:



$$(CN)_3\begin{cases}Cl\\Cl\\Cl\end{cases}\quad (CN)_3\begin{cases}NH_2\\Cl\\Cl\end{cases}\quad (CN)_3\begin{cases}NH_2\\NH_2\\Cl\end{cases}\quad (CN)_3\begin{cases}NH_2\\NH_2\\NH_2\end{cases}$$

cyanuric chloride intermediate compounds melamine.

The second of these intermediate compounds was identified as Liebig's chlorcyanamide (1834, *A.* 10, 43), and its phenylamido- analogue as the compound described by Laurent (1848, *A. Ch.* [3] 22, 97) under the name chlorcyanilide.

The alkyl melamines obtained by these reactions were at once compared with those which Hofmann had himself prepared sixteen years before by desulphurisation of substituted thioureas, and were found to be metamerides. Here, then, were two metameric series of alkyl melamines just as there are two series of alkyl cyanates and cyanurates and their thio- analogues. One might be normal and the other iso-, corresponding to the normal and iso- cyanates or cyanurates. Their constitution was now to be solved. It was feared that the action of water would give no clue to the structure of these compounds, because on the assumption of either constitution cyanuric acid and amine would probably be produced. Thus:

$$\underset{\text{alkyl-}n\text{-melamine}}{(CN)_3 3NHMe} + 3H_2O = \underset{\text{cyanuric acid}}{(CN)_3 3OH} + \underset{\text{amine}}{3NH_2Me}$$

$$\underset{\text{alkyl-iso-melamine}}{(CNMe)_3 3NH} + 3H_2O = \underset{\text{cyanuric acid}}{(CO)_3 3NH} + \underset{\text{amine.}}{3NH_2Me}$$

It is true that in the one case the acid at first formed ought to be normal and in the other iso-, but all experience had shown that, whatever might be the constitution of the acid in the first moment of its existence, it was always found when examined to be one and the same cyanuric acid. Experiment confirmed this expectation, and it became necessary to seek some other method.

This was found by Hofmann in 1885 (*B.* 18, 2781) in a reaction between cyanuric chloride and secondary amines. In this reaction neither melamine nor its primary alkyl derivatives, but secondary alkyl melamines were produced — Hexa-alkyl Melamines. These were prepared, and it was seen that an examination of the decomposition products when acted upon by water would decide whether they were normal or iso- compounds. Thus:

$$\underset{\text{alkyl-}n\text{-melamine}}{(CN)_3 3NMe_2} + 3H_2O = \underset{\text{cyanuric acid}}{(CN)_3 3OH} + \underset{\text{secondary amine}}{3NHMe_2}$$

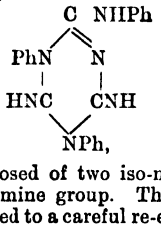
$$\underset{\text{alkyl-iso-melamine}}{(CNMe)_3 3NMe} + 3H_2O = \underset{\text{methyl-iso-cyanurate}}{(CO)_3 3NMe} + \underset{\text{monamine.}}{3NH_2Me}$$

Here was a distinction that could be observed, and experiment showed that the first equation represents the reaction which takes place. The new alkyl melamines are to be regarded, then, as normal derivatives, and the iso- structure is reserved for the metameric compounds derived from substituted ureas.

What, then, is the constitution of melamine itself? When the close analogy existing between the reactions by which the normal alkyl melamines are produced, and that by which melamine itself may be obtained is perceived, there cannot remain much doubt as to its normal constitution, thus:—

$$(CN)_3Cl_3 + 3H(NMe_2) = (CN)_3 3NMe_2 + 3HCl$$
$$(CN)_3Cl_3 + 3H(NHMe) = (CN)_3 3NHMe + 3HCl$$
$$(CN)_3Cl_3 + 3H(NH_2) = (CN)_3 3NH_2 + 3HCl$$

Moreover the normal constitution of cyanuric chloride must not be forgotten. From it are derived only normal ethers, and from normal ethers, as Hofmann himself shows, cyanuric chloride may be reproduced by the action of phosphorus pentachloride. Two subsequent memoirs (*B.* 18, 3217; 19, 2061) contain a description of many new derivatives of normal and iso-cyanuric acid and melamine. Residues in the position which Rathke afterwards proposed to designate by the denomination *eso* are shown to exist in some of these complex derived compounds. This is notably the case with the triphenylmelamine which Hofmann designates unsymmetrical, and which Rathke would term diesotriphenylmelamine. It has the formula



and is composed of two iso-melamine and one normal melamine group. The cyanuric ethers were submitted to a careful re-examination in the first of these papers, and their melting-points and boiling-points re-determined and corrected, and in most cases their crystalline form submitted to exact measurements.

The question of the constitution of cyanuric acid was considered by Hofmann mainly in one of the memoirs already referred to (*B.* 18, 2791). It was pointed out in the first place that the constitution of the normal and iso- series of alkyl derivatives is established beyond question by the perfectly distinct products which they give when subjected to the decomposing action of water. The normal ethers break down into cyanuric acid and alcohol, the iso- ethers into carbon dioxide and amine. So far, then, as the decomposition of the ethers is evidence, cyanuric acid is a normal compound. But, on the other hand, no one has succeeded in preparing normal ethers from cyanuric acid. Iso- ethers, as in the methods of Wurtz and Habich and Limpricht, are always obtained. So far, then, as the formation of the ethers is evidence, cyanuric acid is an iso-compound. Consideration of these reactions leaves the question an open one. Other reactions must be studied. It is argued that cyanuric acid is iso- because of its formation from urea and certain allied compounds; but this assumes a constitution for urea which is by no means finally established; and which, indeed, as Hofmann points out, has been directly questioned. Again to cyanuric acid is assigned the iso- structure, because of its homology with cyanic acid, which is assumed to be iso-. If cyanic acid were really iso- this argument would have great weight; but Hofmann showed, especially by means of its close analogy to normal thio-cyanic acid, that cyanic acid is probably normal in constitution. It is admitted, however, by Hofmann that in order to explain all the reactions, whichever view be accepted, an intra-molecular rearrangement has sometimes to be assumed. For instance, maintaining the normal hypothesis such a change has to be supposed in the case of the reactions of Wurtz and Habich and Limpricht. It is shown, however, that instances of this change from normal to iso- are of frequent occurrence, whereas there is scarcely a case on record—only one which Hofmann himself in a later memoir pointed out—of the opposite change. This then is an argument in favour of the normal hypothesis. But perhaps the strongest of all arguments in support of the normal view is the relation of cyanuric acid to cyanuric chloride. This chloride is, for reasons already given, unquestionably a normal compound. Now phosphorus pentachloride behaves towards normal cyanuric ethers in a manner precisely parallel to its action, as shown by Beilstein, on cyanuric acid itself. In both cases cyanuric chloride results. Again, from cyanuric chloride and alcohol (sodium ethylate) normal ether is obtained, and in the parallel reaction between cyanuric chloride and water (sodium hydroxide) cyanuric acid results. Thus:—

$$(CN)_3 3OR' + 3PCl_5 = (CN)_3Cl_3 + 3POCl_3 + 3R'Cl$$
$$(CN)_3 3OH + 3PCl_5 = (CN)_3Cl_3 + 3POCl_3 + 3HCl$$

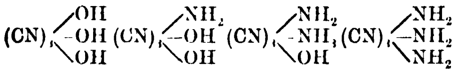
and

$$(CN)_3Cl_3 + 3R'OH = (CN)_3 3OR' + 3HCl$$
$$(CN)_3Cl_3 + 3HOH = (CN)_3 3OH + 3HCl.$$

This analogy receives important support from the corresponding thio- derivatives. It is scarcely conceivable that intramolecular change takes place in one series of these reactions and not in the other, and indeed the composition of the chloride of iso-cyanuric acid is probably such that it would be impossible for it by metastasis to be converted into cyanuric chloride; at all events Hofmann shows that the action of phosphorus pentachloride on iso- ether leads to the formation of a chloride having an altogether different composition. In another memoir in 1886 (*B.* 19, 2084) Hofmann continues this discussion. Klason in the meantime had offered another explanation of Rathke's dicyandiamide and thiocyanic acid reaction, which led to the normal and not the iso- structure for thio-ammeline. Hofmann adopted this. With regard to the use of more than one formula as suggested by Rathke, Hofmann can only admit this practice if it be meant to imply that a compound behaves in one reaction as if it had one constitution, and in another reaction as if its constitution were a different one. The identity of a substance requires that in its quiescent state it be regarded as one and the same thing. The only way out of the difficulty with regard to the constitution of cyanuric acid is to adopt that formula which explains the most reactions, and to assume in the others that metastasis takes place. Hofmann therefore adopts the view that cyanuric acid is a normal or hydroxyl compound.

There now remain to be considered a series of important communications from the Swedish chemist, P. Klason (or Claësson, as it is written in the Swedish memoirs). The field independently worked out by this observer is covered very largely by that of Hofmann, and has already been noticed. This is true also with regard to the view to be taken of the constitution of cyanic and cyanuric acids and melamine. The leading points which remain must now be briefly stated.

In an early communication in 1885 (*B.* 18, 496 R.) some important improvements were suggested in the preparation of cyanuric chloride, and the discovery of Cyanuric Iodide was announced. A series of normal melamines was described a little later (*B.* 18, 497 R.), and it was shown that thio-ammeline was normal and not iso-, as Rathke had maintained. Klason proved this by its synthesis from Liebig's chlorcyanamide (normal diamido-cyanuric chloride), by the action of sodium sulphydrate. The fact that cyanamide by polymerisation gives ordinary normal melamine leads to the view that it also is normal (*B.* 18, 499 R.). On the other hand Klason considered the only known series of alkyl cyanamides to be iso- compounds because they polymerise to alkyl iso- melamines. Maintaining the normal structure for cyanic and cyanuric acids Klason (1886, *J. pr.* 33, 126) submitted the reasoning of Nencki and the more recent arguments of Rathke to a detailed criticism. It was shown that another formula can be ascribed equally well to acetoguanidine, and that this leads to the normal formula for cyanuric acid. This is the case also with Rathke's reaction between dicyandiamide and thiocyanic acid, for Klason maintained that the diamide is a normal and not an iso- compound. The case of Bamberger's reaction is admittedly different. In order to explain that reaction, metastasis has undoubtedly to be assumed. Subsequent examination of the melam compounds by Klason (1886, *J. pr.* 33, 285) showed that ordinary melam is a mixture of true melam and a new compound melem, and that ordinary ammelide is a mixture of melanurenic acid and ammeline. It was therefore proposed to apply the name ammelide to melanurenic acid, in which case the compounds between cyanuric acid on the one hand and melamine on the other would be as follows: –



$$(CN)_3\begin{cases}OH\\OH\\OH\end{cases}\quad(CN)_3\begin{cases}NH_2\\OH\\OH\end{cases}\quad(CN)_3\begin{cases}NH_2\\NH_2\\OH\end{cases}\quad(CN)_3\begin{cases}NH_2\\NH_2\\NH_2\end{cases}$$

cyanuric acid ammelide ammeline melamine.

MONOCYANOGEN GROUP.

Normal cyanic acid CNOH *i.e.* (C:N).OH.

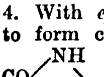
Formation.–1. By the action of heat on cyanuric acid (Wöhler, *G. A.* 71, 95; 73, 157; *P.* 1, 117; Liebig a. Wohler, *P.* 20, 369).—2. In place of cyanuric acid a mixture of P_2O_5 and urea may be employed (Weltzien, *A.* 107, 219) or a mixture of uric acid with MnO_2 or H_2SO_4 (Dobereiner, *G. A.* 74, 121), or mercuric urate may be heated alone.– 3. Cyanic acid is also formed when ethyl thiocarbamate is subjected to distillation. $CO.NH_2.SEt = CNOH + EtSH$ (Debus, *A.* 72, 1; 75, 127; 82, 253).

Cyanic acid cannot be isolated by treatment of its metallic or alkyl salts with hydrous acids or water, for the moment it is liberated it takes up the elements of water and appears as NH_3 and CO_2.

Preparation.- Anhydrous cyanuric acid is heated nearly to redness in a current of CO_2. This is conveniently accomplished in a tube bent at right angles, the charged arm of which can be placed in a combustion furnace. The vapour of cyanic acid is led into a suitable condenser surrounded by a freezing mixture. More or less polymeric cyamelide is always formed and condenses as a snow-white solid in the cooler parts of the tube (Wohler) (Baeyer, *A.* 114, 156).

Properties.– A thin colourless liquid which reddens litmus and has an extremely pungent odour suggestive of glacial acetic acid. The vapour causes a copious flow of tears and the liquid applied to the skin quickly raises a blister. S.G. (0°) 1·140; (−20°) 1·156 (Troost a. Hautefeuille, *J.* 1868, 314). V.D. 1·50 (calc. = 1·49) (T. a. H.). H.C 98,470 (T. a. H.). Cyanic acid changes readily into the isomeric cyamelide or 'insoluble cyanuric acid.' At 0° this transformation takes place quietly in the course of an hour, but at higher temperatures the action becomes explosive. The heat evolved by this atomic rearrangement is 17,630 gram-units (T. a. H., *J.* 1869, 99). In ice-water cyanic acid dissolves without decomposition until a certain degree of concentration is attained.

Reactions.—1. In presence of *triethyl phosphine* it polymerises to cyanuric acid (Hofmann, *C. S. Mem.* 13, 322).—2. Acted on by *water* it immediately splits into NH_3 and CO_2.—3. *Alcohol* reacts on cyanic acid forming allophanic ether $2CNOH + EtOH = CO.NH_2.NH.COOEt$.—4. With *epichlorhydrin* C_3H_5OCl it combines to form chloroxypropyl carbamic anhydride



$$CO\begin{cases}NH\\O\end{cases}\!\!\!-C_3H_5Cl$$

(Thomsen, *B.* 11, 2136).– 5. By the action of *aldehyde* trigenic acid is produced $2CNOH + CH_3CHO = C_4H_7N_3O_2 + CO_2$ (Liebig a. Wohler, *A.* 59, 296; Herzig, *M.* 2, 398).—6. *Sodium amalgam* reacts on CNOK, producing formamide (Basarow, *B.* 4, 409).—7. When dry HCl is passed over CNOK or better CNOAg cyamelide is formed and a liquid cyanic acid hydrochloride CNOH, HCl distils over (Wöhler, *A.* 45, 357).—8. With *chloral* cyanic acid vapour combines to form cyanic acid chloral $(CCl_3CHO)_2CNOH$, and with chloral hydrocyanide it also combines to form the compound $(CCl_3CHO,HCN)CNOH$ (Bischoff, *B* 5, 86; Cech, *B.* 8, 1174; 9, 1253; 10, 880; Wallach, *B.* 8, 1327).

HALOGEN DERIVATIVES.

Cyanogèn chloride CNCl *i.e.* (C:N).Cl.

Formation.–By the action of Cl on aqueous hydrocyanic acid (Berthollet, *A. Ch.* 1, 35, Gay-Lussac, *A. Ch.* 90, 200), or on certain metallic cyanides in presence of water (Serullas, *A. Ch.* [2] 35, 291, 337; *cf.* Wohler, *A.* 73, 219; Cahours a. Cloez, *A.* 90, 97; Cloez, *A.* 102, 354; Klein, *A.* 74, 85; Martius, *A.* 109, 79; Langlois, *A. Ch.* [3] 61, 481).

Preparation.—About 15 grams of $Hg(CN)_2$ are placed in a 3-litre bottle and partly covered with water. Cl is then led in till the whole of the air is displaced, and the bottle is set aside in a dark place for 24 hours. The colour of the Cl gradually disappears, its place being taken by colourless gaseous cyanogen chloride. Several such bottles may be charged and set aside at the same time. For most purposes the gas thus prepared may be at once made use of. If, however, it is desired to isolate the pure chloride the bottle must be placed in a freezing mixture, when crystals of CNCl form, and these by a series of operations are separated in a pure state (Serullas) (Wohler). Explosions having sometimes occurred by the above method (Weith, *B.* 7, 1745), the reaction between aqueous HCN kept in a freezing mixture and Cl is preferred by some chemists (Gautier, *A.* 141, 122). In any case the greatest care is requisite, on account of the extremely poisonous nature of this gas, to prevent its escape into the atmosphere of the laboratory.

Properties.—At ordinary temperatures it is a colourless gas with a pungent odour and irritating action on the eyes. Exceedingly poisonous. At —12° to —15°, or at 0° under a pressure of 4 atmospheres, it condenses to a colourless liquid, and at −18° it crystallises in prisms. V.D. = 2·124 (calc. = 2·128) (Salet, *A.* 136, 144; *cf.* Wurtz, *A.* 79, 284; Regnault, *J.* 1863, 65, 67, 70). C.H. (Berthelot, *J.* 1871, 79; 1874, 114). Polymerises spontaneously but gradually into $(CN)_3Cl_3$. S. 25; 50 (ether), 100 (alcohol). The aqueous solution does not redden litmus, and gives no pp. with $AgNO_3$.

Reactions.—1. *Potassium* heated in CNCl gas gives KCN and KCl, and *antimony* in a similar manner forms a chloride and liberates cyanogen. 2. With aqueous KHO it is converted into CNOK and KCl.—3. *Alcohols* dissolve CNCl, and on standing a reaction gradually takes place with the formation, among other products, of carbonic and carbamic ethers (Wurtz).—4. With *sodium alkylate* CNCl reacts, forming, in the first instance, normal cyanic ethers, which, however, immediately polymerise to the corresponding cyanuric compounds (Cloëz, *C. R.* 44, 482; Hofmann a. Olshausen, *B.* 3, 271).—5. With *ammonia* cyanamide and NH_4Cl are formed, and in the same manner *alkyl ammonias* form alkyl cyanamides (Cloëz a. Cannizzaro, *A.* 78, 229; 90, 95).

Combinations.—1. With other halogen compounds: $SbCl_5CNCl$ (Klein, *A.* 74, 87); BCl_3CNCl (Martius, *A.* 109, 79); $Fe_2Cl_6\,2CNCl$ (K.); $TiCl_4CNCl$ (Wohler, *A.* 73, 220); EtCNCNCl (Henke, *A.* 106, 286); the compound $(CNCl)_2HCN$ (Wurtz, *A.* 79, 281) is said not to exist (Vogt, *A.* 155, 170).—2. With NH_2OH, HCl, PH_3HI, $CO2NH_2$, &c. (Traube, *B.* 18, 462).

Cyanogen bromide CNBr *i.e.* (C:N).Br.

Formation.—By the action of Br on $Hg(CN)_2$ (Serullas, *A. Ch.* [2] 34, 100; 35, 294 a. 315) or on HCNAg (Lowig, *Das Brom und seine chemischen Verhaltnisse*, Heidelberg, 1829, 69), or on a cold solution of KCN (Langlois, *A. Ch.* [3] 61, 482).

Preparation.—When 1 part of Br is allowed to flow gradually on 2 parts of $Hg(CN)_2$ in a retort surrounded with ice CNBr and $HgBr_2$ are formed with great evolution of heat. The CNBr sublimes in needles, contaminated at first with free Br, but ultimately the Br flows back and enters completely into combination. Gentle heat is then applied, and the CNBr sublimed into a receiver surrounded with ice (Serullas).

Properties.—CNBr sublimes in colourless needles, which afterwards change to cubes (S.). [+4°] (Lowig); [above 16°] (S.); [not even at 40°] (Bineau, *A. Ch.* [2] 68, 425); [48°] (Senier, *priv. com.*); [52°] (Mulder, *R.* 4, 151). (61°) (750 mm.) (M.). H.F. (Berthelot, *J.* 1871, 80). Vapour pungent and irritating, resembling CNCl. V. sol. H_2O and alcohol. Forms a crystalline hydrate less fusible than the anhydrous compound.

Reactions.—1. *Heated* in a closed tube from 130°-140° it is converted into $(CN)_3Br_3$.—2. With KHOAq it forms KBr, KCN, and $KBrO_3$ (S.)(L.). 3. *Ammonia gas* reacts with the formation of $CNNH_2$ and NH_4Cl.

Cyanogen iodide CNI *i.e.* (C:N).I.

Formation.—By the action of I on mercuric, silver, or other metallic cyanides (Davy, *G. A.* 54, 384; Wohler, *G. A.* 69, 281; Serullas, *A. Ch.* [2] 27, 184; 29, 184; 31, 100; 35, 293 a. 344; Van Dyk, *R. P.* 21, 223). CNI sometimes occurs as an impurity in commercial iodine (Scanlan, *C. S. Mem.* 3, 321; F. Meyer, *Ar. Ph.* [2] 51, 29; Klobach, *Ar. Ph.* [2] 60, 34).

Preparation.—1. Iodine is dissolved in a warm conc. solution of KCN until the liquid, on cooling, solidifies to a crystalline mass. On gently heating the CNI sublimes, and it may be purified by recrystallisation from alcohol or ether (Liebig, *Chim. Org.* 1, 180).—2. 2 pts. of iodine dissolved in ether are added to 1 pt. of $Hg(CN)_2$. Reaction takes place, and the CNI goes into solution in the ether, from which it may be obtained by evaporation (Linnemann, *A.* 120, 36).

Properties.—Long, delicate, colourless needles, or from its solution in alcohol or ether in four-sided laminæ (Herzog, *Ar. Ph.* [2] 61, 129). It has a pungent, penetrating odour and acrid taste. It is very poisonous. Sol. water, more sol. alcohol, still more sol. ether and volatile oils. No one has hitherto succeeded in converting it into the polymeric $(CN)_3I_3$. H.F. (Berthelot, *J.* 1871, 79; 1874, 114) (*cf.* E. Meyer, *J. pr.* [2] 36, 292).

Reactions.—1. KHO reacts, forming KCN, KI, and KIO_3 (Serullas).—2. NH_3 converts it into $CNNH_2$ and NH_4I.—3. With ZnR'_2 or AlR'_3 alkyl nitriles and metallic iodides are formed (Calmels, *Bl.* 43, 82).—4. It dissolves in alkaline sulphites with the formation of HI, HCN, and alkaline sulphates (Strecker, *A.* 148, 95).

Combinations.—When 4 pts. of I are dissolved in a solution of 1 pt. of KCN in 2 pts. of water long colourless crystals separate, which after recrystallisation from ether have the composition KI,4CNI,4aq. [120°-130°] (Langlois, *A. Ch.* [3] 60, 220).

METALLIC DERIVATIVES *v.* CYANATES, p. 297.

ALKYL DERIVATIVES. *Normal cyanic ethers.* Normal cyanic ethers have never been isolated. The reaction between sodium alcoholate and cyanogen chloride (Cloez, *C. R.* 44, 482), which was supposed to yield normal cyanic ethers, proved when further investigated, both in the methyl series (Hofmann a. Olshausen, *B.* 3, 271) and in the ethyl series (Mulder, *R.* 2, 133), to give no cyanic ether, but instead a mixture of alkyl cyanurate and amido- derivatives. There is not much doubt that in this reaction normal cyanic ethers are formed in the first instance, but they polymerise almost immediately to their cyanuric homologues (*cf.* Ponomareff, *B.* 15, 515; Mulder, *R.* 1, 210; 3, 306).

ALKOYL DERIVATIVES.

Acetyl cyanate $C_3H_3NO_2$ *i.e.* (C:N).OAc. Silver cyanurate acts upon acetyl chloride, forming what is probably a polymeric form of this compound. When this is subjected to distillation liquid acetyl cyanate or cyanogen acetate is obtained, together with acetonitrile and cyanogen. Water decomposes it into acetamide and CO_2 (Schutzenberger, *A.* 123, 271).

Normal thiocyanic acid *v.* THIOCYANIC ACID.

Normal cyanamide CH_2N_2 *i.e.* $(C:N).NH_2$.

Formation.—1. By the action of CNCl, CNBr, or CNI on NH_3. $CNCl + 2NH_3 = CNNH_2 + NH_4Cl$ (Bineau, *A. Ch.* [2] 67, 368; 70, 251; Cloez a. Cannizzaro, *A.* 78, 229).—2. $CNNNa_2$ is the end product of the reaction between NH_2Na and CO_2,

(*a*) $NH_2Na + CO_2 = NH_2.CO.ONa$,

(*b*) $NH_2.CO.ONa = CNONa + H_2O$,

(*c*) $CNONa + NH_2Na = CNNNa_2 + H_2O$

(Beilstein a. Geuther, *A.* 108, 93; Drechsel, *J. pr.* [2] 16, 203).—3. By the action of sodium on urea, ammonium carbamate, or ammonium carbonate $CO(NH_2)_2 + Na = CNNH_2 + H + NaHO$ (Fenton, *C. J.* 41, 262).—4. By desulphurisation of thio-urea by means of HgO. $CS(NH_2)_2 - H_2S = CNNH_2$ (Volhard, *J. pr.* [2] 9, 25; Baumann, *B.* 6, 1371; Mulder a. Smit, *B.* 7, 1636).

Preparation.—Moist freshly ppd. mercuric oxide, which has been purified by boiling with NaHOAq and then with water, is added in small portions at a time to an unsaturated cold solution of thio-urea in water. Excess of HgO is avoided, otherwise insoluble mercuric cyanamide is formed (Engel, *Bl.* 24, 273). The operation is continued until all the thio-urea is desulphurised, which may be ascertained by the liquid ceasing to give a black pp. when a drop of it is tested with NH_3AgNO_3. The sulphide pp. is then filtered off and the filtrate concentrated as quickly as possible by evaporation, the latter part of the process being conducted in a vacuum over H_2SO_4. From the residue, ether extracts cyanamide and leaves dicyandiamide, which is also formed, undissolved (Volhard; Drechsel, *J. pr.*

[2] 11, 298; 21, 79). Another method employs an alcoholic instead of an aqueous solution of thio-urea (Baumann, *B.* 6, 1376; Prätorius, *J. pr.* [2] 21, 131). It is noteworthy that pure thio-urea does not admit of complete desulphurisation in this reaction, the presence of traces of such a substance as $CNSNH_4$, however, renders the action of the HgO perfectly easy (Traube, *B.* 18, 461).

Properties.– Cyanamide is a white crystalline compound [40°]. When melted, however, it may be cooled far below 40° without solidification taking place. This, however, is at once effected by contact with a pointed solid body. V. sol. water, alcohol, and ether; sl. sol. CS_2, $CHCl_3$, and benzene. Heated above 40° it passes into the homologous *n*-di-cyandiamide $(CN)_2 2NH_2$, and at about 150° it solidifies with evolution of heat, forming *n*-tri-cyantriamide or melamine, together with other products (Drechsel, *J. pr.* [2] 13, 331). Cyanamide suffers this intramolecular condensation with great readiness. The change takes place at once when a solution containing ammonia is evaporated, or, again, when an alcoholic solution is heated together with phenol. In these cases the dicyanogen homologue results. More slowly cyanamide polymerises into dicyandiamide simply by standing.

Reactions.—1. $CNNH_2$ is reduced by *nascent H* (Zn and HCl), with the formation of NH_3 and $MeNH_2$. (*a*) $CNNH_2 + H_2 = CNH + NH_3$, (*b*) $CNH + H_4 = MeNH_2$ (Drechsel).—2. *Heated with KNO_2Aq* a violent reaction takes place with evolution of nitrogen and production of carbon dioxide and di-cyandiamide $4CNNH_2 + 4KNO_2 = 2K_2CO_3 + H_2O + 8N + (CN)_2 2NH_2$ (Drechsel).—3. The addition of HNO_3 to an ethereal solution causes it to combine with a molecule of water, forming urea, which, being insoluble in the ether, ppts. Sulphuric, phosphoric, salicylic and lactic acids behave in a similar manner (Baumann, *B.* 6, 1373; Pratorius).—4. With *haloid acids* direct addition compounds are formed.—5. With H_2S, or better with yellow *ammonium sulphide*, cyanamide combines to form thio-urea.—6. $AgNO_3$ reacts on $CNNH_2$ forming AgCN and a yellow flocculent pp. $CNNAg_2$. $3CNNH_2 + 4AgNO_3 = CNNAg_2 + AgCN + AgNO_3 + CO_2 + 6N + 3H_2O$. 7. With *glycocoll* $CNNH_2$ yields glycocyamine (Strecker, *Handw. d. Chem.* [2] 3, 286), and with methyl-glycocoll $CH_2(NHMe)COOH$ it forms creatine.—8. $CNNH_2$ dissolves in *aldehyde*, and after standing the mixture becomes resinous, and contains the compound $(CN)_3 3NC_2H_4$, aq triethylidene melamine (Knop, *A.* 131, 253).—9. Heated with *oxalic ether* formomelamine $(CN)_3(NH_2)_2NHCHO$ results.—10. At high temperatures it combines with NH_4Cl, forming guanidine hydrochloride $C(NH)2NH_2,HCl$, and with NH_3OHCl forming oxyguanidine hydrochloride $C(NOH)2NH_2,HCl$. In the same manner, with $(CN)SNH_4$ guanidine thiocyanate $C(NH)2NH_2,HSCN$ is obtained. — 11. $CNNH_2$ combines directly with CN, forming a yellow powder (Hofmann, *J.* 1861, 530).—12. With CNOK cyanamide combines to form monopotassium amidodicyanate $(CN)_2.NH_2.OK$. — 13. *Alloxanthin* reacts on cyanamide, forming iso-uric acid (Mulder, *B.* 6, 1236).—14. With *guanidin* it combines to form diguanid.

Combinations.—*With haloid acids* (Drechsel, *J. pr.* [2] 11, 315; Mulder, *B.* 7, 1634). $CNNH_2 2HCl$ is produced as a crystalline pp. when anhydrous HCl is conducted into an ethereal solution of cyanamide. V. sol. water, sol. alcohol, insol. ether. If to the alcoholic solution of this compound HgO be added, and the clear solution evaporated, crystals of $CNNH_2HgCl_2 3aq$ are obtained. They are v. sol. water. The corresponding HBr compound exists, $CNNH_2 2HBr$ (D.).– *With chloral.* The two compounds combine directly to form chloral cyanamide, $CCl_3CHO,CNNH_2$ (R. Schiff a. Fileti, *B.* 10, 426).

METALLIC DERIVATIVES.

Formation.—*Monometallic salts.* Aqueous or alcoholic solutions of alkalis or earths or alkyl alkalis, act on cyanamide, giving mono-derivatives $NaOEt + CNNH_2 = CNNHNa + EtOH$ (Drechsel, *J. pr.* [2] 11, 307; 16, 205; 21, 81). *Di-metallic salts.*—1. By the action of heat on earthy and other metallic cyanates, $Ca(CNO)_2 = CNNCa + CO_2$ (Drechsel).—2. By heating pure $Ba(CN)_2$ in a current of N. $Ba(CN)_2 + N = CNNBa + CN$ (Drechsel).—3. $CNNK_2$ is among the products of the heating of KCN or CNOK with NaHO.

$2KCN + 4NaHO = CNNK_2 + Na_2CO_3 + Na_2O + H_4$ (Drechsel).—4. By heating together NH_2Na and CNONa.

$CNONa + NH_2Na = CNNNa_2 + H_2O$ (Drechsel)

Properties.—*Sodium salt* CN.NHNa. Fine crystalline powder. V. e. sol. water, sol. alcohol, insol. ether. It absorbs oxygen and CO_2 with avidity. With CO_2 it forms a salt of cyanamido-carboxylic acid $CO\begin{matrix}\diagup NHCN\\ \diagdown ONa\end{matrix}$, an isomeride of cyanic acid. With ethyl chloroformate ClCOOEt sodium cyanamide combines to form cyanamido-dicarboxylic ether $CN.N(COOEt)_2$. Isocyanic and isothiocyanic ethers combine with CNNHNa with the production of amido-dicyanic derivatives $CNNHNa + CONEt = CN.(NNa).CO.NHEt$. *Calcium salt* $(CN.NH)_2Ca$. This may be prepared by acting on $CNNH_2$ with $Ca(HO)_2Aq$. From an aqueous solution crystals of the salt $CNN(CaOH)_2 6aq$ have been obtained (G. Meyer, *J. pr.* [2] 18, 425).

Disodium salt $CN.NNa_2$. Heated with charcoal it gives NaCN. *Sodium potassium salt* CN.NKNa (Drechsel). *Calcium salt* CN.NCa. Decomposed by water with formation of mono-salt (Drechsel; G. Meyer). *Mercuric salt* CN.NHg″ (Engel, *Bl.* [2] 24, 273). *Lead salt* CN.NPb. Ammoniacal solution of $CNNH_2$ gives a lemon-yellow pp. of this compound with $Pb(C_2H_3O)_2$. *Copper salt* CN.NCu (Engel). *Silver salt* $CN.NAg_2$. An amorphous yellow pp. V. e. sol. HNO_3, insol dil. ammonia. Explodes quietly when heated (Drechsel; Beilstein a. Geuther, *A.* 108, 99).

ALKOYL DERIVATIVES.

Acetyl cyanamide $C_3H_4N_2O$ *i.e.* (C⋮N).NHAc.

Formation.—1. By the action of acetyl chloride on cyanamide in ethereal solution (Drechsel, *J. pr.* [2] 11, 314).—2. Sodium acetyl cyanamide is formed by treatment of sodium cyanamide with acetic anhydride. This is converted into the silver salt from which the silver is removed by H_2S (Mertens, *J. pr.* [2] 17, 7).

Properties.—A syrupy acid liquid. V. sol.

water, alcohol, ether, and chloroform, insol. benzene. When heated the liquid undergoes a violent reaction and is converted into a solid (polymeric ?) mass (Mertens).

Combinations with metals.—Sodium salt (CN)NAcNa. A hygroscopic crystalline powder. Sol. alcohol, insol. ether. Heated it splits into acetonitrile and sodium cyanate. *Silver salt* (CN)NAcAg. Prepared by precipitating (CN)NAcNa,Aq with $AgNO_3$. A white crystalline powder. Insol. water, v. sol. ammonia. Heated it evolves acetonitrile.

Diacetyl cyanamide $C_5H_6N_2O_2$ *i.e.* (C:N).NAc_2. Rhombic plates decomposing at 65°. Insol. water, v. sl. sol. alcohol, sol. ether. Obtained by acting upon CNNHAc in ethereal solution with AcCl (Mertens).

Butyryl cyanamide $C_5H_8N_2O$ *i.e.* (C:N)NH(C_4H_7O). The sodium salt is formed by acting on (CN)NHNa with $(C_4H_7O)_2O$ in ethereal solution. This salt is insol. ether, but sol. water. From the aqueous solution $AgNO_3$ ppts. the silver salt, which is sol. ammonia, and from which the free cyanamide may be obtained.

Isovaleryl cyanamide $C_6H_{10}N_2O$ *i.e.* (C:N)NH(C_5H_9O). Formed in a similar way to acetyl-cyanamide. An acid syrup, sol. water, alcohol, and ether. Converted by heat, with a violent reaction, into a solid (polymeric ?) mass. *Silver salt* (CN)N(C_5H_9O)Ag.

Benzoyl cyanamide $C_8H_6N_2O$ *i.e.* (C:N)NHBz.

Formation.—By the action of benzoyl chloride BzCl on sodium cyanamide (CN)NHNa in ethereal solution.

Properties.—Unstable. Decomposes into CO_2, (CN)NH, and BzCN. Digested in ethereal solution it polymerises to tribenzoyl normal melamine (Gerlich, *J. pr.* [2] 13, 272).

Lactocyanamide v. Lactic acid.

Succincyanimic acid
Succincyanimide } *v.* Succinic acid.
Succincyamide

Carboxylic derivatives.

Cyanamidocarbonic acid v. Cyanamidocarboxylic acid.

Cyanamidodicarbonic acid v. Cyanamidodicarboxylic acid.

Condensed cyanamido compounds.

Cyanogen cyanamide C_2HN_3 *i.e.* (C:N).NH.(C:N). Not known in a free state. CN.NK.CN is formed by the action of KHO on CNCl or paracyanogen, or by fusing paracyanogen with KCN. Needles. CN.NAg.CN is ppd. when $AgNO_3$ is added to an aqueous solution of CN.NK.CN (Bannow, *B.* 4, 254).

Isocyanic acid CHNO *i.e.* (C:O):NH. Isocyanic acid has not hitherto been isolated, neither are halogen or metallic derivatives known.

Alkyl derivatives. *Isocyanic ethers.*

Formation.—1. By distilling alkyl sulphate of potassium with potassium cyanate. Part of the isocyanic ether formed polymerises to isocyanurate (Wurtz, *A. Ch.* [3] 42, 43).—2. From carbamines by oxidation with HgO (Gautier, *A.* 149, 313).—3. By the action of alkyl iodides on silver cyanate (Brauner, *B.* 12, 1874).—4. By distilling alkyl-chloroformamides with lime (Gattermann, *A.* 244, 36).

Properties.—Low-boiling pungent irritating liquids.

Reactions.—(Wurtz.) 1. Polymerise gradually on standing into the corresponding isocyanuric ethers.—2. *Hydrolysis* when heated with dilute KHOAq, they break down into CO_2 and amines CONEt + H_2O = CO_2 + NH_2Et. When treated with water alone the reaction does not go so far, CO_2 and *s*-dialkyl urea being formed, 2CONEt + H_2O = CO_2 + $CO(NHEt)_2$. — 3. With *alcohols* they combine to form alkyl-carbamic ethers, thus: CONEt + EtHO = NHEt.CO.OEt. — 4. *Organic acids* react giving acid amides and carbonic acid CONEt + AcOH = CO_2 + AcNHEt. — 5. Anhydrides yield tertiary amides and carbonic acid CONEt + Ac_2O = CO_2 + Ac_2NEt. — 6. NH_3 and prim. and sec. amines combine to form substituted ureas CONEt + $NHEt_2$ = NEt_2.CO.NHEt. — 7. The oxygen may be replaced by sulphur by treatment with P_2S_5, mustard oils or isothiocyanic ethers being formed.

Methyl isocyanate C_2H_3NO *i.e.* (C:O):NMe. (37°) (Gattermann): (44°) (Wurtz; Gautier).

Ethyl isocyanate C_3H_5NO *i.e.* (C:O):NEt. (60°). S.G. 0·898 (Wurtz). The pure ether does not polymerise on standing, but the presence of NaOEt quickly transforms it into isocyanurate (Hofmann, *J.* 1861, 515; *A.* 103, 353; 115, 275). In the same manner NEt_3, with which it does not combine, determines its polymerisation (Hofmann, *J.* 1862, 335). *Hydrochloride* CONEt,HCl is formed by acting directly on the ether with HCl gas, or by distillation of $CO(NHEt)_2$,HCl (Habich a. Limpricht, *A.* 109, 107). Highly pungent irritating liquid (95°) (H. a. L.). (108°–112°) (Gal, *Bl.* 6, 435). Water decomposes it with violence into NH_2EtHCl and CO_2. *Hydrobromide* CONEt.HBr (118°–122°) (Gal).

Isopropyl isocyanate C_4H_7NO *i.e.* (C:O):N(C_3H_7). (67°) (Hofmann, *B.* 15, 756).

Isobutyl isocyanate C_5H_9NO *i.e.* (C:O):N(C_4H_9). (110°) (Brauner, *B.* 12, 1877).

Tertiary butyl isocyanate C_5H_9NO *i.e.* (C:O):N(CMe_3). The action of isobutyl chloride on silver cyanate gives small quantities of isobutyl isocyanate together with *tert*butyl isocyanate, a polymeric butyl isocyanate, isobutylene, cyanic, and cyanuric acids. The polymeric isobutyl isocyanate remains behind after *tert*butyl isocyanate is distilled off, and may be separated from the other products by solution in ether (Brauner, *B.* 12, 1874). Aromatic pungent liquid. (85·5° cor.). S.G. º 0·8676. Does not solidify at −25°.

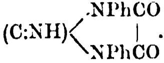
Isoamyl isocyanate $C_6H_{11}NO$ *i.e.* (C:O):N(C_5H_{11}). (100°) (Wurtz, *J.* 1849, 428); (134°–135°) (Custer, *B.* 12, 1330). Insol. and lighter than water. Solution of PEt_3 in ether polymerises it to isocyanurate (Custer).

Hexyl isocyanate $C_7H_{13}NO$ *i.e.* (C:O):N(C_6H_{13}). (above 100°) (Cahours a. Pelouze, *J.* 1863, 526).

Allyl isocyanate C_4H_5NO *i.e.* (C:O):N(C_3H_5). (82°) (Cahours a. Hofmann, *A.* 102, 297).

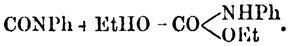
Benzyl isocyanate v. Benzyl cyanate.

Phenyl isocyanate C_7H_5NO *i.e.* (C:O):NPh (Hofmann, *A.* 74, 9 a. 33; *J.* 1858, 348; *B.* 3, 655; 18, 764).

Formation.—1. By the distillation of melanoximide  $(C{:}NH)\left\langle\begin{array}{l}NPhCO\\ \quad|\\ NPhCO\end{array}\right.$.—2. By distilling oxanilide $C_2O_2(NHPh)_2$ with P_2O_5.—3. By the action of P_2O_5 on di-phenyl-urea. —4. By distilling alkyl carbanilate NHPh.CO.OEt with P_2O_5. 5. By acting on melted $CO(NHPh)_2$ or NH_2Ph,HCl with $COCl_2$ (Hentschel, *B.* 17, 1284).

Properties.—Highly pungent irritating liquid (166° at 769 mm.). S.G. 1·092 at 15°. V.D. 4·09 (calc. 4·13).

Reactions. 1. In presence of PEt_3, or C_5H_5N (Snape, *C. J.* 49, 254), it polymerises to diphenyl-isodicyanate $(C{:}O)_2(NPh)_2$.—2. Heated with certain dry salts, CH_3COOK, HCOOK, or Na_2CO_3 it polymerises to isocyanurate. 3. It forms addition compounds with Cl and Br.—4. *Water* immediately converts it into carbanilide and CO_2, thus: $2CONPh + H_2O = CO_2 + CO(NHPh)_2$. 5. *Alcohols* and *phenols* combine with phenylisocyanate to form alkyl phenylcarbamates



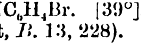
$$CONPh + EtHO = CO\left\langle\begin{array}{l}NHPh\\ OEt\end{array}\right.$$

. — 6. *Ammonia amines* and *amides* form with it substituted ureas. 7. Aniline is produced when it is heated with *zinc-dust.* 8. Heated with Ac_2O; acetanilide and CO_2 are among the products. —9. In presence of $AlCl_3$ it combines with C_6H_6 and its homologues to form benzanilide, &c. CONPh + PhH = BzNHPh (Leuckart, *B.* 18, 875). In the same manner it combines with *phenolic ethers* (Leuckart a. Schmidt, *B.* 18, 2338).

Combinations.—$CONPh,Cl_2$: unstable crystals (Gumpert, *J. pr.* [2] 32, 291).—$CONPh,Br_2$ (G.). CONPh,HCl.: crystalline [45°] (Hentschel, *B.* 18, 1178).

p-Bromophenyl isocyanate $CONC_6H_4Br$. [39°]. (226°). Sol. ether (Dennstedt, *B.* 13, 228).

o-Tolyl isocyanate C_8H_7NO *i.e.* $(C{:}O){:}N(C_7H_7)$.

Formation.—By acting on ethyltolylcarbamate  $CO\left\langle\begin{array}{l}NHC_7H_7\\ OEt\end{array}\right.$ with P_2O_5 (Girard, *B.* 6, 445).

Properties.—Liquid. (186°). Powerful pungent odour. Polymerises into a solid modification by the action of PEt_3 (Nevile a. Winther, *B.* 12, 2324).

p-Tolyl isocyanate C_8H_7NO *i.e.* $(C{:}O){:}N(C_7H_7)$. Similar to *o*-ether. Formed also from *p*-toluidine and $COCl_2$ (Kuhn a. Henschel, *B.* 21, 505). (185°). Water decomposes it into di-*p*-tolyl-urea and CO_2 (Hofmann, *B.* 3, 656).

Mesityl isocyanate $C_{10}H_{11}NO$ *i.e.* $(C{:}O){:}N(C_9H_{11})$. Disagreeable smelling liquid. (218°–220°) (Eisenberg, *B.* 15, 1017).

Cumyl isocyanate $C_{11}H_{13}NO$ *i.e.* $(C{:}O){:}N(C_{10}H_{13})$ (Raab, *B.* 8, 1151).

(α)-*Naphthyl isocyanate* $C_{11}H_7NO$ *i.e.* $(C{:}O)N(C_{10}H_7)$. Pungent irritating liquid. (269°–270°) (Hofmann, *B.* 3, 658).

Diphenyl isocyanate $C_{13}H_9NO$ $(C{:}O){:}N(C_{12}H_9)$ (Zimmermann, *B.* 13, 1965).

Diphenylene diisocyanate $CO{:}N.C_6H_4.C_6H_4.N{:}CO$ [122°] (Snape, *C. J.* 49, 255).

Thioisocyanic acid derivatives *v.* THIOISOCYANIC ACID.

Isocyanamide (C:NH):NH. This compound has not been isolated, but its alkyl derivatives exist.

ALKYL DERIVATIVES.

Formation.—1. By the action of CNCl on primary amines (Cloëz a. Cannizzaro, *A.* 90, 95). 2. By the desulphurisation of alkyl thio-ureas $NH_2.CS.NHMe - H_2S = (CNMe)NH$.

Properties.—Neutral syrupy liquids. By repeated evaporation of their aqueous solutions, polymerisation to the corresponding isomelamines takes place (Baumann, *B.* 6, 1372; Klason, *Bihang till K. Svenska Vet. Akad. Hand.* 1885, [10] No. 7).

Methylisocyanamide $C_2H_4N_2$ *i.e.* (C.NMe):NH (Baumann, *B.* 6, 1372).

Diethylisocyanamide $C_5H_{10}N_2$ *i.e* (C:NEt):NEt.

Formation.—1. (CNEt)NH breaks down when distilled into (CNEt)NEt and a crystalline base, possibly ethyldicyandiamide (Cloez a. Cannizzaro).—2. By the action of $(CN)NAg_2$ on EtI (R. Schiff a. Fileti, *B.* 10, 428).

Properties.—Liquid. (186°) (S. a. F.); (190°) (C. a. C.). By treatment with HCl it yields CO_2, NH_3, and $NHEt_2$.

Allylisocyanamide $C_4H_6N_2$ *i.e.* $(C{:}NC_3H_5){:}NH$.

Formation—(Will, *A.* 52, 15; Robiquet a. Bussy, *J. pr.* 19, 234; Andreasch, *M.* 2, 780).

Properties.—A thick syrupy liquid which gradually crystallises in monoclinic four-sided prisms with ½aq. [100°]. Sol. water, alcohol, and ether. Strong alkaline reaction. Precipitates metallic oxides from solution of their salts and liberates ammonia from its combination with acids. The oxalate is difficultly crystallisable. Its solution gives precipitates with $HgCl_2$ and $PtCl_4$:—$C{:}NC_3H_5{:}NH,HgCl_2$ and $(C{:}NC_3H_5{:}NH)_2PtCl_4$.

Allylethylisocyanamide $C_6H_{10}N_2$ *i.e.* $(C{:}NEt){:}NC_3H_5$.

Properties.—Needles. [100°]. Insol. water, sol. alcohol and ether. Reaction alkaline. Taste bitter. Compounds with $HgCl_2$ and $PtCl_4$:—$(C{:}NEt{:}NC_3H_5)_2 3HgCl_2$ and $(C{:}NEt{:}NC_3H_5)_2PtCl_4$ (Hinterberger, *A.* 83, 316).

Benzylisocyanamide *v.* BENZYLCYANAMIDE.

Dibenzylisocyanamide *v.* DIBENZYLCYANAMIDE.

Phenylisocyanamide $C_7H_6N_2$ *i.e.* (C:NPh):NH

Formation.—(Cloez a. Cannizzaro; Hofmann, *B.* 3, 266; 18, 3220; Berger, *M.* 5, 219 a. 453; Rathke, *B.* 12, 773).

Properties.—Syrup gradually crystallising in presence of alcohol in needles (Feuerlein, *B.* 12, 1602). [47°] (Hofmann). V. sl. sol. water; sol. alcohol and ether. When water is added to the alcoholic solution phenyl-urea, $CO.NHPh.NH_2$, is precipitated. In the same manner in a benzene solution H_2S gives phenyl-thio-urea (Weith, *B.* 9, 820). Silver salt: C:NPh:NAg (Hofmann; Feuerlein; Berlinerblau, *J. pr.* [2] 30, 114). Platinum chloride salts: $(C_7H_6N_2HCl)_2PtCl_4$ (Feuerlein); $(C_7H_6N_2 2HCl)_2PtCl_4$ (Hofmann). With acetamide, among other products, two bases, $C_{39}H_{35}N_{11}$, and $C_{15}H_{16}N_6$, are formed (Berger).

Diphenyl-isocyanamide $C_{13}H_{10}N_2$ *i.e.* (C:NPh):NPh. Formed by the action of CNCl on diphenylamine (Weith, *B.* 7, 848). Rhombohedra. [292°]. Heated with conc. HCl it gives NH_3, $NHPh_2$, and CO_2.

DICYANOGEN GROUP.

Fulminic acid $C_2H_2N_2O_2$. This dibasic acid has not been isolated. A solution in ether is, however, probably obtained when dry HCl is conducted into a mixture of fulminating mercury with that solvent. It forms acid neutral and double salts, all of which are explosive compounds. The mercury and silver compounds have long been known and employed for the filling of percussion caps. The ethereal solution treated with NaHO evolves NH_3, but no amine. When it is shaken with NH_3 isofulminuric acid, fulminuramide, and other products are formed (Ehrenberg, *J. pr.* [2] 30, 55). Dilute H_2SO_4 also sets free fulminic acid in presence of ether, but in this case the products of its decomposition give rise to another series of isomeric modifications (Scholvien, *J. pr.* [2] 32, 181). Only metallic derivatives of fulminic acid are known.

METALLIC DERIVATIVES.

Disodium fulminate $Na_2C_2N_2O_2$ 2aq. Formed from mercuric fulminate suspended in water by the action of sodium amalgam. The liquid concentrated over H_2SO_4 or CaO deposits prismatic crystals of the disodium salt. Explodes when rubbed or heated. H_2O_2 decomposes it with formation of NH_3, CO_2, and HCN (Ehrenberg, *J. pr.* [2] 32, 231).

Disilver fulminate $Ag_2C_2N_2O_2$.

Preparation.—1 pt. of silver is dissolved in 10 pts. of HNO_3 (S.G. 1·36), and the solution poured into 20 pts. of spirits of wine (85-90 p.c.) (Brugnatelli, *A. Ch.* 1798, 27, 331; Gerhardt, *Traité de Chim. Org.* 2, 348). The salt separates in fine needles.

Properties.- S. 36 at 100° (Liebig, *B. J.* 4, 111); v. sl. sol. cold water; v. sol. ammonia. More explosive than the mercury salt.

Reactions.--1. Half of the metal is replaced by treatment with *alkaline chlorides* (Gay-Lussac a. Liebig, *A. Ch.* [2] 25, 285).- 2. *Hydrochloric acid* separates all the silver, but with breaking up of the molecule of the acid (Gay-L. a. L.). When fuming HCl is employed three-quarters of the molecule breaks down into hydroxylamine and formic acid, the other products being CO_2, NH_3, and HCN. With dilute acid more NH_2OH and formic acid are formed, and only traces of NH_3 (Divers a. Kawakita, *C. J.* 45, 15; 47, 69).

Silver sodium fulminate $NaAgC_2N_2O_2$. Small crystalline plates.

Silver potassium fulminate $KAgC_2N_2O_2$. Colourless plates. S. 8 at 100° (Liebig).

Silver hydrogen fulminate $HAgC_2N_2O_2$. Falls as a pulverulent pp. when conc. HNO_3 is added to an aqueous solution of $AgKC_2N_2O_2$ (Liebig).

Zinc fulminate $ZnC_2N_2O_2$ (E. Davy, *B. J.* 12, 120).

Zinc hydrogen fulminate $ZnH_22C_2N_2O_2$ (E. Davy; Fehling, *A.* 27, 130).

Copper fulminate $CuC_2N_2O_2$ (Gladstone, *A.* 66, 1).

Mercuric fulminate $Hg''C_2N_2O_2$.

Preparation.—3 pts. of mercury are dissolved in 36 pts. of HNO_3 (S.G. 1·345) in a large flask without the application of heat. The solution is poured into 17 pts. of spirits of wine (90-92 p.c.) and the mixture returned to the large flask. After a time a violent reaction commences, which is moderated by the addition of more spirits of wine to the extent of another 17 pts. Mercuric fulminate gradually deposits, and is collected and recrystallised from water. It may be also purified by solution in KCN and reprecipitation by means of dilute acids (Howard, *Tr.* 1800; Liebig, *A.* 95, 284; Steiner, *B* 9, 787).

Properties.--Mercuric fulminate crystallises from alcohol in minute octahedra, from water in needles containing ½aq (Schischkow, *A.* 97, 54). S.G. (anhydrous) 4·42 (Berthelot a. Vieille, *A. Ch.* [5] 21, 569). V. sl. sol. cold, more sol. hot water. Explodes by heat, friction or percussion, or by treatment with H_2SO_4. The products of decomposition are Hg, N, and CO. H.C. (Berthelot a. Vieille).

Reactions.- 1. Zn and H_2SO_4, or Sn and HCl, or zinc dust and ammonia, break down the molecule into Hg, CO_2, and NH_3.—2. *Sodium amalgam* converts it into the Na salt. The by-products of this reaction, by treatment with ferrous and ferric oxides yield among other compounds nitroprussides. -3. Heated with water containing Cu or Zn, these metals displace the mercury.—4. *Chlorine* conducted into the salt mixed with water reacts, forming $HgCl_2$, CNCl, and chloropicrin $C(NO_2)Cl_3$ (Kekulé, *A.* 101, 206). 5. *Bromine* in the same manner forms dibromonitroacetonitril CBr_2NO_2CN (Schischkow).—6. Heated for 8 hours with *water* alone, or for a shorter time in presence of NaCl or NH_4Cl, it polymerises to the corresponding fulminurate (Schischkow; Liebig).--7. Mixed with ether it reacts with dry H_2S forming HgS, nitrothioacetamide $CH_2(NO_2)CSNH_2$, oxalic acid and ammonium thiocyanate. In presence of water the products are HgS, ammonium thiocyanate, and CO_2 (Kekulé).—8. Mixed with KHOAq and heated, a pp. of HgO falls.—9. *Ammonia* dissolves mercuric fulminate, but when the solution is heated to 60°-70° a reaction takes place with the production of urea, guanidin, and the compound called fulmitriguanarate. Heated in closed tubes to 70° with alcoholic ammonia the compound fulmitetraguanarate is also formed (Steiner, *B.* 8, 520, 1177; 9, 781). 10. Conc. HCl or HBr react, evolving CO_2, precipitating HgCl and 2 mol. of NH_2OH going into solution. Traces of HCN also occur, but no NH_3 (Steiner, *B.* 16, 1484 a. 2119; Carstanjen a. Ehrenberg, *J. pr.* [2] 25, 232).--11. Dilute HCl in the cold yields formic acid, hydroxylamine and $HgCl_2$ (Ehrenberg, *J. pr.* [2] 30, 41).--12. H_2SO_4 (1 in 5) reacts on warming, forming CO_2, NH_3, NH_2OH, $HgSO_4$, and $Hg_2C_2O_4$ (?) (Ehrenberg a. Carstanjen; Divers a. Kawakita).—13. Conc. HCN dissolves the fulminate, but when the solution is diluted $Hg(CN)_2$ precipitates. -14. Aqueous CNSH reacts, forming CO_2, $Hg(SCN)_2$ and NH_4SCN. With NH_4SCN polymerisation to fulminurate takes place (Ehrenberg, *J. pr.* [2] 30, 62).

Combinations.- With KI: $(HgC_2N_2O_2)_2KI$ (Schischkow). — With KCN: $HgC_2N_2O_2,KCN$ (Steiner, *B.* 9, 786). — With KSCN it forms $HgC_2N_2O_2,KSCN$ (Schischkow).—With $Na_2C_2N_2O_2$: $HgC_2N_2O_2$, $Na_2C_2N_2O_2$, aq (Ehrenberg).

Compound $C_2H_2Hg_4N_2O_8$.

Formation.—This substance, the nature of which is little known, is formed when a cold solution of $Hg(NO_3)_2$ free from fumes of HNO_3 is thrown into alcohol (Cowper, *C. J.* 39, 242).

Properties.—Minute hexagonal plates. Decomposes quickly when gently heated, but if the temperature be suddenly raised to about 130° it explodes. Insol. water, alcohol, and ether. Sol. HCl with decomposition. Sol. and may be recrystallised from dilute H_2SO_4.

Reactions.—1. With H_2SAq the compound yields HgS and mercaptan.—2. Digested with caustic alkalis nitric acid is removed, and the compound $C_2H_2(HgO)_3,H_2O$ remains.—3. Heated with alcohol and HNO_3 it is converted into mercuric fulminate.

Normal amidodicyanic acid $C_2H_3N_3O$ *i.e.* $\mathrm{(HO)C}{<}\!\begin{smallmatrix}\mathrm{N}\\ \mathrm{N}\end{smallmatrix}\!{>}\mathrm{C(NH_2)}$. *Semi-amide of normal dicyanic acid.*

Formation.—1. By heating dicyandiamide with baryta water one of the amido- groups is replaced by hydroxyl (Hallwachs, *A.* 153, 295). 2. By allowing a solution of CNOK to stand together with cyanamide, when direct combination takes place, $NH_2(CN)_2OK$ being formed (Hallwachs).

Properties.—Needles. Monobasic acid. Decomposes carbonates. Heated alone or together with dilute H_2SO_4, it takes up the elements of water, forming biuret, thus: $(CN)_2(NH_2)OH + H_2O = NH_2.CO.NH.CO.NH_2$. In the same manner with $(NH_4)_2S$ thiobiuret is obtained (Baumann, *B.* 8, 709).

Metallic derivatives.

$(CN)_2NH_2OK$. —NaA'.— BaA'_2 3aq. — CuA'_2 4aq. Large blue crystals. V. sl. sol. cold water. Aqueous solution, when boiled, deposits a dark green pp. insol. water, and v. sl. sol. cold acetic acid. This pp. has the composition C_2N_3CuHO *i.e.* (?) $\mathrm{(CN)_2}{<}\!\begin{smallmatrix}\mathrm{NH}\\ \mathrm{O}\end{smallmatrix}\!{>}\mathrm{Cu}$.— $(CN)_2(NH_2)OAg$. Amorphous powder, or from ammoniacal solution in needles. Insol. water.

Alkyl derivatives.

Ethyl amidodicyanate $C_4H_7N_2O_2$ *i.e.* ? $\mathrm{NH_2C}{<}\!\begin{smallmatrix}\mathrm{NEt}\\ \mathrm{N}\end{smallmatrix}\!{>}\mathrm{CO}$. The sodium salt of this compound is formed by direct combination of ethyl isocyanate and normal sodium cyanamide. The free acid decomposes when liberated with formation of cyanamide and other products.

Salts.—(CNCO):NEt.NHNa.—AgA' (Wunderlich, *B.* 19, 449).

Dithiodicyanic acid *v.* Dithiodicyanic acid.

Normal dicyandiamide $C_2H_4N_4$ *i.e.* $\mathrm{(NH_2)C}{<}\!\begin{smallmatrix}\mathrm{N}\\ \mathrm{N}\end{smallmatrix}\!{>}\mathrm{C(NH_2)}$. *Di-amide of normal dicyanic acid.*

Formation.—Cyanamide polymerises to dicyandiamide by long continued evaporation of its aqueous solution (Beilstein a. Geuther, *A.* 108, 99; 123, 241). This change is more readily effected if a little NH_3 is present (Haag, *A.* 122, 22), or dilute alkalis, or even in the cold when concentrated alkalis are employed (Baumann, *B.* 6, 1373).

Properties.—Broad laminæ [205°] (Haag). Sol. water and alcohol. Insol. ether (cyanamide is sol. ether).

Reactions.—1. *Heated* alone one part polymerises to normal melamine, another loses NH_3 and forms melam (Drechsel, *J. pr.* [2] 13, 331).—2. Heated with *water* polymerisation takes place, and at the same time two amidogen groups are replaced by hydroxyl, forming melanurenic acid $(CN)_3(NH_2)(OH)_2$ and NH_3. This acid is also formed by heating dicyandiamide to 120° with a solution of $(NH_4)_2CO_3$.—3. Heated with dilute acids it assumes the elements of water, forming guanylurea $\mathrm{CO}{<}\!\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{NH.C(NH)NH_2}\end{smallmatrix}$. Similarly with H_2S guanylthiourea is produced.—4. With HCl and zinc melamine and NH_3 are formed (*cf.* Bamberger, *B.* 16, 1462).—5. Guanidin hydrochloride, together with CO_2 and NH_3, are formed by heating it with NH_4Cl at 150° (Rathke, *B.* 18, 3107). 6. Heating with $Ba(OH)_2Aq$ one amido group is replaced by hydroxyl, leaving amidodicyanic acid.—7. It combines with CNSH to form thioammeline $\mathrm{(CN)_3}\!\begin{array}{l}\diagup\mathrm{NH_2}\\ -\mathrm{NH_2}\\ \diagdown\mathrm{SH}\end{array}$ (Rathke, *B.* 18, 3102).

Metallic derivatives.

Sodium dicyandiamide $C_2H_3N_4Na$ *i.e.* $(CN)_2(NH_2)NHNa$. A soluble crystalline pp. obtained by mixing together alcoholic solutions of dicyandiamide and sodium ethylate (Bamberger, *B.* 16, 1461).

Dicyandiamido silver nitrate $(C_2H_4N_4)AgNO_3$. Precipitated in minute needles on adding $AgNO_3$ to an aqueous solution of dicyandiamide (Haag).

Silver dicyandiamide $C_2H_3N_4Ag$ *i.e.* $(CN)_2(NH_2)NHAg$. Formed by treating an aqueous solution of dicyandiamido silver nitrate with ammonia.

Alkyl derivatives.

Ethyl dicyandiamide $C_4H_8N_4$ *i.e.* $(CN)_2(NH_2)NHEt$. A weak base formed by distilling ethyl cyanamide (Cloez a. Cannizzaro, *A.* 90, 96). Distils unchanged at 300°. Gives a yellow insoluble platinochloride salt.

Alkoyl derivatives.

Dibenzoyl dicyandiamide $C_{16}H_{12}N_4O_2$ *i.e.* $(CN)_2(NHBz)_2$. Formed by heating tribenzoylmelamine in a current of hydrogen. Crystals. [112°]. V. sol. alcohol, less sol. ether, v. sl. sol. water (Gerlich, *J. pr.* [2] 13, 272).

Isodicyanic acid $C_2H_2N_2O_2$ *i.e.* $(C{:}O)_2(NH)_2$ or $\mathrm{CO}{<}\!\begin{smallmatrix}\mathrm{NH}\\ \mathrm{NH}\end{smallmatrix}\!{>}\mathrm{CO}$. Alkyl derivatives corresponding to this hypothetical acid have been prepared.

Alkyl derivatives.

(?) *Dimethyl isodicyanate* $C_4H_6N_2O_2$ *i.e.* $\mathrm{CO}{<}\!\begin{smallmatrix}\mathrm{NMe}\\ \mathrm{NMe}\end{smallmatrix}\!{>}\mathrm{CO}$. Methyl isocyanate polymerises in presence of PEt_3 to a solid compound [98°] (Hofmann, *B.* 3, 765), which is not identical with either methyl isocyanurate [175°-6°] or methyl cyanurate [135°], and which possibly has the above constitution.

Diphenyl isodicyanate $C_{14}H_{10}N_2O_2$ *i.e.* $\mathrm{CO}{<}\!\begin{smallmatrix}\mathrm{NPh}\\ \mathrm{NPh}\end{smallmatrix}\!{>}\mathrm{CO}$.

Formation.—By polymerisation of phenyl isocyanate in presence of PEt_3 (Hofmann, *A. Suppl.* 1, 57; *B.* 4, 246) or pyridine (Snape, *C. J.* 49, 254).

Properties.—Square tables from alcohol. [175°] Insol. water or ether, v. sl. sol. alcohol.

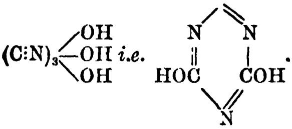
Reactions.—1. Heated it evolves phenyl isocyanate.—2. Heated with *alcohols* it forms alkyl diphenylallophanates CO.NHPh.NPhCOOEt.—3. With *phenol* phenyl-carbanilate is formed NHPh.CO.OPh.—4. Alcoholic *ammonia* reacts with the formation of β-di-phenyl-biuret NHPh.CO.NPh.CO.NH_2.—5. With *aniline* tri-phenyl-biuret results.

Derivative.—Di-*p*-bromo-phenyl isodicyanate $(CO)_2(NC_6H_4Br)_2$ is formed by polymerisation of *p*-bromo-phenyl isocyanate with PEt_3. Laminæ. [199°] (Dennstedt, *B.* 13, 228).

Di-p-tolyl dicyanate $C_2N_2O_2(C_7H_7)_2$. [185°] (Frentzel, *B.* 21, 411). Converted by alcohol into di-*p*-tolyl allophanic ether [111°].

TRICYANOGEN GROUP.

Normal cyanuric acid $C_3H_3N_3O_3$ *i.e.*



$(C⋮N)_3(OH)_3$ *i.e.* . *Tricyanic acid.*

Formation.—1. Dry distillation of uric acid (Scheele, *Opuscula*, 2, 76).—2. By the action of water on $(CN)_3Cl_3$ (Serullas, *A. Ch.* 38, 390).—3. By the action of heat on urea (Wohler, *P.* 15, 622). Instead of urea itself the salts of urea may be employed (Pelouze, *A.* 44, 106; De Vrij, *A.* 61, 249; Wiedemann, *A.* 68, 324).—4. By heating cyamelide with conc. H_2SO_4 (Weltzien, *A.* 132, 222).—5. Cyanuric acid is one of the products of the action of $COCl_2$ on NH_3.—6. The action of heat on xanthogenamide $3CS(NH_2)OEt = (CN)_3(OH)_3 + EtHS$ (Debus, *A.* 72, 18).—7. By the action of HCl on such compounds as melam, melen, melon, melonic hydride, melamine, ammeline, ammelide, pseudothiocyanogen, and thioprussides.—8. From guanamide by oxidation with HNO_3 (Nencki, *B.* 9, 235).—9. From cyanic acid by spontaneous polymerisation together with cyamelide. This may be effected by adding HCl to CNOKAq in presence of ether and agitating. The cyanuric acid is taken up by the ether (Klason, *J. pr.* [2] 33, 129).

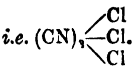
Preparation.—1. Urea is heated till it ceases to give off ammonia, the residue is dissolved in boiling water, and the filtrate left to crystallise on cooling. The crystals so obtained are purified by dissolving them in hot H_2SO_4 and dropping in HNO_3 until the solution is colourless and effervescence has ceased. After cooling the solution is diluted with water when the cyanuric acid falls as a snow-white powder (Wohler a. Liebig).—2. Dry chlorine gas is passed into melting urea, whereupon the mass swells up strongly, gives off fumes of NH_4Cl, together with HCl and N, and is converted into cyanuric acid (Wurtz, *A.* 64, 307).—3. De Vrij (*A.* 61, 248) uses HCl instead of Cl. Serullas prepares the acid from cyanuric chloride, and Merz a. Weith (*B.* 16, 2896) similarly employ cyanuric bromide.

Properties.—Colourless oblique rhombic prisms (from water) containing 2aq, or anhydrous octahedra. Measurements (Keferstein a. Schabus, *P.* 99, 275). Crystals effloresce. By heating to 100°-120°, or by crystallisation from conc. HCl or H_2SO_4, the acid becomes anhydrous (Wöhler, *B. J.* 10, 83; Voit, *A.* 132, 222). S.G. $^{\underline{0}}$ 1·768; $^{\underline{12}}$ 2·500; $^{\underline{24}}$ 2·228; $^{\underline{45}}$ 1·725 (Troost a. Hautefeuille, *J.* 1869, 99; *cf.* Schröder, *B.* 13, 1072). H.C. 250,260 (T. a. H.). S 2·5 cold, more sol. hot water. S. (alcohol) 21°-24°, 0·1 (Senier, *C. J.* 49, 695). Sol. hot HCl, HNO_3, or H_2SO_4, without decomposition unless the heat be prolonged for a considerable time. Absorption spectrum (Hartley, *C. J.* 41, 48). By treatment with PCl_5 cyanuric chloride is formed (Beilstein, *A.* 116, 357).

Test Reactions.—1. Heated in a small tube closed at one end it evolves cyanic acid, the pungent odour of which may be detected even in the case of very minute quantities (Wohler).—2. A fragment of the acid is dissolved in dilute ammonia and a drop of ammonio-sulphate of copper solution added. On stirring a beautiful pink copper salt is precipitated (Wohler).—3. A saturated solution of the acid in cold conc. NaHOAq becomes thick with suspended crystals of the tri-sodium salt on heating (Hofmann, *B.* 3, 770).

HALOGEN DERIVATIVES.

Cyanuric chloride $C_3N_3Cl_3$ *i.e.*



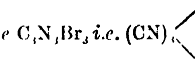
$(CN)_3Cl_3$.

Formation.—1. By the action of anhydrous Cl on anhydrous HCN in presence of sunlight (Serullas, *A. Ch.* [2] 35, 291 a. 337; Liebig, *P.* 20, 369; 34, 604).—2. By treatment of cyanuric acid with PCl_5 (Beilstein, *A.* 116, 357).

Preparation.—The employment of the method of Serullas has given rise to several improvements, chiefly with the view of preventing the formation of persistent double compounds of HCl and HCN. The HCN is dissolved in anhydrous ether, into which the Cl is led (Gautier, *A.* 141, 122), or the ether may be advantageously replaced by chloroform, in which Cl is more soluble, for an excess of this agent leads to a better result. 70 p.c. of the theoretical yield was thus obtained by Klason (*Bihang till K. Svenska Vet. Akad. Handl.* 1885, 10, No. 5). Another plan to attain this end is to ensure excess of Cl from the commencement. The chloroform surrounded by a freezing mixture is first saturated with chlorine, and then a mixture of Cl and HCN is passed slowly in until after some 24 hours the evolution of HCl ceases, and the whole of the HCN is converted into chloride. A portion of the cyanuric chloride in most instances separates from the $CHCl_3$ during the operation in beautiful crystals. The remainder is obtained by distilling off the chloroform (Fries, *C. J.* 49, 739).

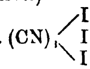
Properties.—Colourless crystals. Measurements (Hofmann (Fock), *B.* 19, 2063). [146°] (Hofmann). (190°) (Serullas). V.D. 6·35 (calc. 6·39) (Bineau, *A. Ch.* [2] 68, 424). Odour resembling mice. Exceedingly irritating to the eyes. Very poisonous.

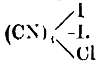
Reactions.—1. Cold *water* has little or no action on $(CN)_3Cl_3$. By long boiling with water or quickly in presence of alkalis it is converted into cyanuric acid (Serullas).—2. *Alcohols* and *phenol* behave similarly to water, cyanuric acid and alkyl chlorides being formed (Klason).—3. KHS in the same manner gives trithiocyanuric acid (Hofmann, *B.* 18, 2201).—4. *Ammonia* or *amines* react successively, forming normal mono- and di-amide- chlorides, and finally normal melamines (Hofmann, *B.* 18, 2774; Klason, *J. pr.* [2] 33, 294).—5. Cyanuric chloride reacts on the anhydrous *sodium salts of organic acids* giving acid chlorides and sodium cyanurate (Senier, *C. J.* 49, 312). - 6. *Benzamide* is converted by cyanuric chloride into benzonitrile, and the water thus liberated acts on the chloride forming cyanuric acid and HCl (Senier).

Cyanuric bromide $C_3N_3Br_3$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}Br\\Br.\\Br\end{array}\right.$

Formation. 1. By the action of bromine on anhydrous HCN (Serullas, *P.* 14, 446; Ponomareff, *B.* 18, 3261; Merz a. Weith, *B.* 16, 2894).—2. By heating an ethereal solution of CNBr to 130°–140° (Eghis, *B.* 2, 159). Pure CNBr does not polymerise. Polymerisation may, however, be effected by passing HBr through an ethereal solution of CNBr when the less soluble polymeride comes out in crystals (Ponomareff).

Properties. -Amorphous white powder. At 300° it melts with decomposition. Insol. cold water, cold alcohol, ether, and benzene. Heated with water or alcohol it is converted into cyanuric acid. With acetic acid it yields cyanuric acid and acetyl bromide (Ponomareff).

Cyanuric iodide $C_3N_3I_3$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}I\\I.\\I\end{array}\right.$ Obtained by double decomposition between $(CN)_3Cl_3$ and HI in the cold (Klason, *Bihang till K. Svenska Vet. Akad. Handl.* 1885, 10, No. 5). A dark brown insoluble powder which at 200° decomposes into paracyanogen and iodine. Heated with water at 125° it splits into HI and cyanuric acid.

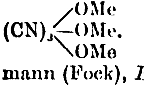
Cyanuric chloro iodide $C_3N_3I_2Cl$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}I\\-I.\\Cl\end{array}\right.$ An intermediate product between cyanuric chloride and iodide, also formed in the preparation of the latter (Klason).

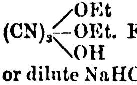
METALLIC DERIVATIVES *v.* CYANURATES.

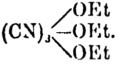
ALKYL DERIVATIVES.

Formation. By the action of CNCl on sodium alcoholates, in which case normal cyanic ether is probably first formed and then polymerised (Hofmann a. Olshausen, *B.* 3, 271). CNBr or $(CN)_3Br_3$ is conveniently substituted for CNCl in this reaction (Ponomareff, *B.* 18, 3261; Klason, *J. pr.* [2] 33, 131).

Reactions.—1. By *distillation* they are converted into the corresponding iso- ethers (Hofmann a. Olshausen).—2. Heated with dilute *alkalis* they assume the elements of water, and break down into alcohols and cyanuric acid.

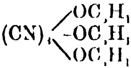
Trimethyl cyanurate $C_6H_9N_3O_3$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}OMe\\-OMe.\\OMe\end{array}\right.$ Needles. Measurements (Hofmann (Fock), *B.* 19, 2065). [135°]. (265°) (Hofmann). Sl. sol. cold, v. sol. hot water (Hofmann a. Olshausen). PCl_5 reacts forming $(CN)_3Cl_3$ (Hofmann, *B.* 18, 2799). With $HgCl_2$ it gives $C_6H_9N_3O_3HgCl_2$ (Ponomareff, *B.* 18, 3266).

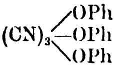
Diethyl-cyanuric acid $C_7H_{11}N_3O_3$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}OEt\\-OEt.\\OH\end{array}\right.$ Formed by the action of $Ba(HO)_2Aq$ or dilute NaHOAq on the triethyl ether (Ponomareff, *B.* 18, 3267; Hofmann, *B.* 19, 2077; Mulder, *R.* 4, 91). Crystalline powder [160–180] (Hofmann). Sublimes above 200° with decomposition. Sl. sol. cold water or alcohol, insol. ether. Warmed with acids cyanuric acid is set free. The barium salt crystallises with 3aq from concentrated or with 12aq from dilute solutions. V. sol. water. The lead salt is insol. water.

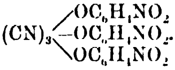
Triethyl cyanurate $C_9H_{15}N_3O_3$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}OEt\\-OEt.\\OEt\end{array}\right.$

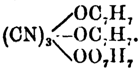
Properties.—An oily liquid crystallising at 0° (Mulder, *B.* 15, 70; *R.* 1, 195; 2, 133; 4, 91; Ponomareff, *B.* 15, 513). [29°–30°] (Hofmann, *B.* 19, 2074). (275°) (Klason, *J. pr.* [2] 33, 131). S. 0·7 in cold water. V. sol. alcohol, ether, $CHCl_3$, and CS_2. The aqueous solution at 0° deposits a crystalline hydrate containing 12aq (Mulder). With $HgCl_2$ it forms the crystalline double salt $C_9H_{15}N_3O_3HgCl_2$ (Ponomareff), and with Br the compound $C_9H_{15}N_3O_3Br_6$ (Mulder).

Reactions. 1. Heated to 180°–200° it is converted into triethyl isocyanurate. -2. Conc. HCl sets free cyanuric acid. -3. Dilute NaHO or $Ba(HO)_2$ removes one of the Et radicles forming diethyl-cyanuric acid.—4. PCl_5 reacts with formation of $(CN)_3Cl_3$.—5. Heated with conc. NH_3Aq to 170°–180° amidogen replaces ethoxyl groups, ammeline and melamine being formed.

Tri-iso-amyl cyanurate $C_{18}H_{33}N_3O_3$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}OC_5H_{11}\\-OC_5H_{11}.\\OC_5H_{11}\end{array}\right.$ Syrupy liquid. Undergoes intramolecular change above 360° (Klason).

Triphenyl cyanurate $C_{21}H_{15}N_3O_3$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}OPh\\-OPh.\\OPh\end{array}\right.$ Needles. [224°]. Distils unchanged. Insol. water and ether, sol. benzene. Conc. HCl at 180° causes it to combine with the elements of water and break down into phenol and cyanuric acid (Hofmann a. Olshausen; Hofmann, *B.* 18, 765; 19, 2083; Klason, *Bihang till K. Svenska Vet. Akad. Handl.* 1885, 10, No. 7).

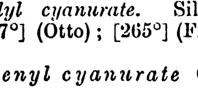
Tri-p-nitrophenyl cyanurate $C_{21}H_{12}N_6O_9$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}OC_6H_4NO_2\\-OC_6H_4NO_2.\\OC_6H_4NO_2\end{array}\right.$ Pale yellow tables. [194°] (Otto, *B.* 20, 2236).

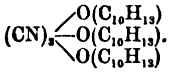
Tri-tolyl cyanurates $C_{24}H_{21}N_3O_3$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}OC_7H_7\\-OC_7H_7.\\OC_7H_7\end{array}\right.$

Tri-o-tolyl cyanurate. Pale yellow needles. [152°] (Otto).

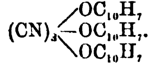
Tri-m-tolyl cyanurate. Colourless microscopic needles. [225°] (Otto).

Tri-p-tolyl cyanurate. Silky colourless needles. [207°] (Otto); [265°] (Frentzel, *B.* 21, 411).

Tri-eugenyl cyanurate $C_{33}H_{33}N_3O_6$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}O(C_{10}H_{11}O)\\-O(C_{10}H_{11}O).\\O(C_{10}H_{11}O)\end{array}\right.$ Pale yellow microscopic laminæ. [122°] (Otto).

Tri-thymyl cyanurate $C_{33}H_{39}N_3O_3$ *i.e.*  $(CN)_3\left\langle\begin{array}{l}O(C_{10}H_{13})\\-O(C_{10}H_{13}).\\O(C_{10}H_{13})\end{array}\right.$ Pale yellow crystalline powder. [151°] (Otto).

Tri-naphthyl cyanurates $C_{33}H_{21}N_3O_3$ *i.e.*


$(CN)_3\begin{array}{l}\diagup OC_{10}H_7\\ - OC_{10}H_7.\\ \diagdown OC_{10}H_7\end{array}$

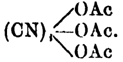
Tri-(α)-naphthyl cyanurate. Greenish yellow powder, decomposing when heated without having a distinct melting-point.

Tri-(β)-naphthyl cyanurate. Light green powder (Otto).

Alkoyl derivatives.

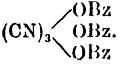
Formation.—By the action of alkoyl chlorides on silver cyanurate (Ponomareff, *B.* 18, 3273; Senier, *C. J.* 49, 313).

Tri-acetyl cyanurate $C_9H_9N_3O_6$ *i.e.*


$(CN)_3\begin{array}{l}\diagup OAc\\ - OAc.\\ \diagdown OAc\end{array}$

Acetyl chloride and silver cyanurate are brought together in presence of ether, the mixture is afterwards evaporated, and the residue crystallised from chloroform. Minute crystals. [170°] with decomposition. Insol. ether; sl. sol. $CHCl_3$. Sol. warm water with decomposition into acetic and cyanuric acids (Ponomareff). A very similar compound to this was obtained by the action of AcCl on CNOAg in the preparation of cyanogen acetate or acetyl cyanate (Schutzenberger, *A.* 123, 271).

Tri-benzoyl cyanurate $C_{24}H_{15}N_3O_6$ *i.e.*


$(CN)_3\begin{array}{l}\diagup OBz\\ - OBz.\\ \diagdown OBz\end{array}$

Benzoyl chloride and silver cyanurate are heated together in closed tubes at 100°. The contents are extracted with $CHCl_3$, which on evaporation deposits tribenzoyl cyanurate in needles. On heating it decomposes. Sl. sol. $CHCl_3$; insol. ether. Warmed with water it decomposes into cyanuric and benzoic acids (Senier).

Normal thiocyanuric acid *v.* Thiocyanuric acid.

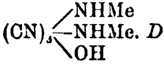
Normal amido-cyanuric acid. *Ammelide. Melanurenic acid* (*v.* Ammelide).

Normal diamido-cyanuric acid. *Ammeline* (*v.* Ammeline).

Halogen derivatives *v.* Ammeline.

Alkyl derivatives.

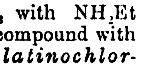
Di-methyl-di-amido cyanuric acid. Dimethyl ammeline $C_5H_9N_5O$ *i.e.*


$(CN)_3\begin{array}{l}\diagup NHMe\\ - NHMe.\\ \diagdown OH\end{array}$ *Dimethyl amide of cyanuric acid.*

Formed by heating di-methyl di-amido cyanuric chloride with dilute acids or by heating it with water at 200° (Hofmann, *B.* 18, 2770), or by heating tri-chloroacetonitril with aqueous methylamine at 120° (Weddige, *J. pr.* [2] 33, 89). Crystalline pp. Heated it decomposes without melting. V. sl. sol. boiling water; insol. alcohol and ether; sol. NaHOAq. Possesses acid and basic properties. $(C_5H_9N_5O,HCl)_2PtCl_4$.

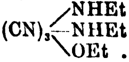
Ethyl diamido-cyanurate v. Ammeline.

Ethyl ethylamido-amido-cyanurate. Diethyl-ammeline $C_7H_{13}N_5O$ *i.e.*


$(CN)_3\begin{array}{l}\diagup NH_2\\ - NHEt.\\ \diagdown OEt\end{array}$

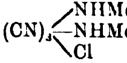
Obtained by acting on $(CN)_3Cl_3$ with NH_2Et and treatment of the resulting compound with HCl (Hofmann, *B.* 18, 2776).—*Platinochloride* $(C_7H_{13}N_5O,HCl)_2PtCl_4$.

Ethyl di-ethyl-di-amido-cyanurate. Tri-ethyl-ammeline $C_9H_{17}N_5O$ *i.e.*


$(CN)_3\begin{array}{l}\diagup NHEt\\ - NHEt\\ \diagdown OEt\ .\end{array}$

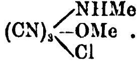
Formed by heating tri-ethyl-melamine with HCl (Hofmann, *B.* 2, 604). Syrupy liquid. Pt. salt:—$(C_9H_{17}N_5O,HCl)_2PtCl_4$.

Di-methyl-di-amido-cyanuric chloride $C_5H_8N_5Cl$ *i.e.*


$(CN)_3\begin{array}{l}\diagup NHMe\\ - NHMe.\\ \diagdown Cl\end{array}$

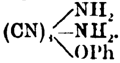
Prepared by the action of $(CN)_3Cl_3$ on a solution of methylamine in methyl alcohol (Hofmann, *B.* 18, 2766; Klason, *Bihang till K. Svenska Vet. Akad. Handl.* 1885, 10, No. 7). Needles. [241°]. Insol. water, alcohol, and ether. Soluble with partial decomposition in glacial acetic acid. Reacts with water, forming dimethylammeline. Ammonia converts it into dimethylmelamine; methylamine turns it into trimethyl melamine.

Methylamido-methoxy-cyanuric chloride $C_5H_7N_4OCl$ *i.e.*


$(CN)_3\begin{array}{l}\diagup NHMe\\ - OMe\ .\\ \diagdown Cl\end{array}$

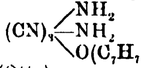
Formed in the same reaction with the last-mentioned compound (Hofmann, *B.* 18, 2771). Needles. [155°]. Sol. alcohol and ether.

Phenyl diamidocyanurate. Phenyl ammeline $C_9H_9N_5O$ *i.e.*


$(CN)_3\begin{array}{l}\diagup NH_2\\ - NH_2.\\ \diagdown OPh\end{array}$

Insoluble white crystalline powder. [245°] (Otto, *B.* 20, 2240).

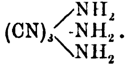
o-Tolyl diamidocyanurate. Tolyl ammeline $C_{10}H_{11}N_5O$ *i.e.*


$(CN)_3\begin{array}{l}\diagup NH_2\\ - NH_2\ .\\ \diagdown O(C_7H_7)\end{array}$

White crystalline solid. [225°] (Otto).

Alkoyl derivatives *v.* Benzoyl ammeline.

Normal cyanuramide. *Normal Melamine.* $C_3H_6N_6$ *i.e.*


$(CN)_3\begin{array}{l}\diagup NH_2\\ - NH_2.\\ \diagdown NH_2\end{array}$

Formation.—1. Is one of the by-products in the preparation of melam by the action of heat on ammonium thiocyanate (Liebig, *A.* 10, 18, 53, 312; Volhard, *J. pr.* [2] 9, 29; Claus, *A.* 179, 121; *B.* 9, 1915; Jaeger, *B.* 9, 1554).—2. By the action of aqueous ammonia at 100° on $(CN)_3Cl_3$ (Hofmann, *B.* 18, 2765; Klason, *Bihang till K. Svenska Vet. Akad. Handl.* 1885, 10, No. 7).—3. From trimethyl thiocyanurate by the action of concentrated ammonia at 180° (Hofmann, *B.* 18, 2759).—4. Cyanamide polymerises by the action of heat to dicyanamide, and then passing to the trimolecular grouping, part forms melamine, and part with evolution of ammonia condenses to melam (Drechsel, *J. pr.* [2] 13, 331).—5. Melamine thiocyanate is formed when strong ammonia is made to act on pseudo-cyanogen sulphide at 160° (Ponomareff, *J. R.* 8, 215).—6. By the action of heat on guanidine carbonate in presence of phenol (Nencki, *J. pr.* [2] 17, 235). 7. Cyanmelamidine breaks down when heated with HCl into melamine and HCN (Byk, *J. pr.* [2] 20, 346).

Preparation.—Trimethyl thiocyanurate is inclosed in a tube with an excess of concentrated solution of ammonia, and heated at a temperature of 180° for several hours. The temperature must not vary much, for if 200° or so is attained hydroxyl compounds are formed, and if it falls much below 180° the reaction is incomplete, and the melamine will be found to contain sulphur, rendering a second treatment with ammonia necessary. When the operation is successful the tube on cooling will contain an upper layer of methyl mercaptan, while below in the aqueous portion large colourless crystals of melamine will have made their appearance. It may be further purified by recrystallisation from water (Hofmann).

Properties. — Monoclinic prisms (Weibull, *J. pr.* [2] 33, 292). Heated gently it sublimes. V. sl. sol. cold, v. sol. hot water. V. sl. sol. hot alcohol, sol. hot glycerin. Powerful base forming salts and decomposing many metallic salts.

Reactions.—1. *Heated* to low redness two molecules combine with evolution of $3NH_3$ to form mellon $(CN)_3:(NH)_3:(CN)_3$.—2. Heated with dilute HNO_3 the amidogen groups are successively replaced by hydroxyl giving ammeline, ammelide, and finally cyanuric acid (Knapp, *A.* 21, 256).—3. Fused with KHO potassium mellon and potassium cyanate are formed.—4. $(CN)_3Cl_3$, AcCl, and Ac_2O are without action on melamine (Senier, *B.* 19, 312).

Combinations. - B',HCl 1½aq: needles (Liebig, *A.* 26, 187; Byk, *J. pr.* [2] 20, 345). —$(B'HCl)_2,PtCl_4$ 2aq (Hofmann, *B.* 18, 2760; Klason, *J. pr.* [2] 33, 293).—$B'_2H_2SO_4$ 2aq also with 1½aq and 3aq. V. sl. sol. cold water. Test for melamine (Drechsel, *J. pr.* [2] 13, 332; Byk; Jaeger, *B.* 9, 1555).—B',H_2SO_4. Short rhombic prisms. Decomposed by water (Nencki, *J. pr.* [2] 17, 237).—$B'_2H_2C_2O_4$. V. sl. sol. water. - B'HSCN: prismatic crystals. V. sl. sol. cold water (Claus, *B.* 9, 1915; Ponomareff, *J. R.* 8, 215).- B'$AgNO_3$. Crystalline pp. sol. hot water and ammonia (Liebig; Byk). — B'2$AgNO_3$: needles (Zimmermann).

METALLIC DERIVATIVES.

By treating $(CN)_3(NH_2)_3 2AgNO_3$ with ammonia a compound said to be *diargentomelamine*

$(CN)_3\begin{matrix}\diagup NHAg\\ -NHAg\\ \diagdown NH_2\end{matrix}$ is obtained (Zimmermann).

ALKYL DERIVATIVES.

Formation. - 1. By the final action of amines on $(CN)_3Cl_3$ (Hofmann; Klason).- 2. By the action of secondary amines on $(CN)_3Cl_3$ (Hofmann, *B.* 18, 2773).—3. By the action of amines on trialkyl thiocyanurates (Hofmann).

Reactions.—1. *Water* (dilute acids) decomposes alkyl-melamines into cyanuric acid and amines.

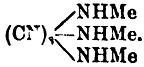
$(CN)_3(NHEt)_3 + 3HOH = (CN)_3(OH)_3 + 3NH_2Et$

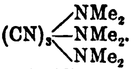
and

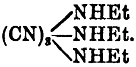
$(CN)_3(NEt_2)_3 + 3HOH = (CN)_3(OH)_3 + 3NHEt_2$

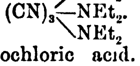
(Hofmann, *B.* 18, 2773).

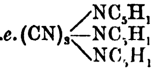
Dimethylcyanuramide. Dimethylmelamine. $C_5H_{10}N_6$ *i.e.* $(CN)_3\begin{matrix}\diagup NHMe\\ -NHMe\\ \diagdown NH_2\end{matrix}$. From diamido-cyanuric chloride by the action of ammonia. Crystalline base. Sol. water, sl. sol. alcohol and ether (Hofmann, *B.* 18, 2768).

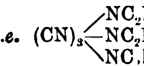
Trimethylcyanuramide. Trimethylmelamine $C_6H_{12}N_6$ *i.e.*  $(CN)_3\begin{matrix}\diagup NHMe\\ -NHMe\\ \diagdown NHMe\end{matrix}$. Base. [115°]. V. sol. water and alcohol.—$(B'HCl)_2PtCl_4$. Prisms.—$B'(HCl)_2,PtCl_4$: long needles (Hofmann, *B.* 18, 2763 a. 2767; Klason, *J. pr.* [2] 33, 293).

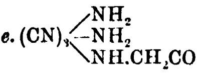
Hexamethylcyanuramide. Hexamethylmelamine $C_9H_{18}N_6$ *i.e.*  $(CN)_3\begin{matrix}\diagup NMe_2\\ -NMe_2\\ \diagdown NMe_2\end{matrix}$. Base. Needles. [171°-172°]. — $(B'HCl)_2PtCl_4$: long needles. Sl. sol. water; sol. alcohol (Hofmann).

Triethylcyanuramide. Triethylmelamine $C_9H_{18}N_6$ *i.e.*  $(CN)_3\begin{matrix}\diagup NHEt\\ -NHEt\\ \diagdown NHEt\end{matrix}$. Base. Needles (from water) or prisms (from alcohol). [73°-74°]. Sl. sol. boiling water. Sol. alcohol, ether, and benzene.—$(B'HCl)_2PtCl_4$: insoluble needles. —$B'_2(HCl)_2PtCl_4$.—B'_2AgNO_3 (Hofmann, *B.* 18, 2775; Klason, *J. pr.* [2] 33, 294).

Hexaethylcyanuramide. Hexaethylmelamine $C_{15}H_{30}N_6$ *i.e.*  $(CN)_3\begin{matrix}\diagup NEt_2\\ -NEt_2\\ \diagdown NEt_2\end{matrix}$. Liquid. Sol. alcohol and hydrochloric acid. Base. $(B'HCl)_2PtCl_4$. Crystalline. Sol. alcohol, sl. sol. water.—$B'HCl,AuCl_3$: needles. V. sl. sol. water and alcohol (Hofmann, *B.* 18, 2778).

Tripiperidyl-cyanuramide. Tripiperidylmelamine $C_{18}H_{30}N_6$ *i.e.*  $(CN)_3\begin{matrix}\diagup NC_5H_{10}\\ -NC_5H_{10}\\ \diagdown NC_5H_{10}\end{matrix}$. Base. Needles. [213°].—$(B'HCl)_2PtCl_4$. Heated with HCl at 150° it is decomposed into piperidine and cyanuric acid (Hofmann, *B.* 18, 2780).

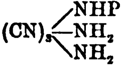
Triethylidencyanuramide. Triethylidenmelamine $C_9H_{12}N_6$ *i.e.*  $(CN)_3\begin{matrix}\diagup NC_2H_4\\ -NC_2H_4\\ \diagdown NC_2H_4\end{matrix}$. Formed by the action of CH_3CHO on $CNNH_2$. Sol. alcohol; insol. water, CS_2, $CHCl_3$, benzene, and aniline (Knop, *A.* 131, 253).

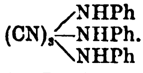
Cyanuramido acetic acid. Melamyl acetic acid. $C_5H_8N_6O_2$ *i.e.*  $(CN)_3\begin{matrix}\diagup NH_2\\ -NH_2\\ \diagdown NH.CH_2COOH\end{matrix}$.

Formation.—By the action of chloro-acetic acid in presence of sodium ethylate on cyanamide (Drechsel, *J. pr.* [2] 11, 332).

Properties.—Crystalline powder. Decomposes without melting when heated. V. sl. sol. water, insol. alcohol and ether. Sol. alkaline solutions. Combines with bases, acids, and salts.

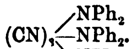
Combinations.—K salt: sol. water. Combines readily with CO_2.—B'HCl: needles; v. sl. sol. water; insol. hydrochloric acid.- B'HNO_3aq: laminæ. — B'$AgNO_3$aq: needles. — $B'_2H_2SO_4$: large prisms.

Phenylcyanuramide. Phenylmelamine $C_9H_{10}N_6$ *i.e.*  $(CN)_3\begin{matrix}\diagup NHPh\\ -NH_2\\ \diagdown NH_2\end{matrix}$. Formed by heating diamidocyanuric chloride with aniline at 150°. Prisms. [284°]. Sol. alcohol. $(B'HCl)_2PtCl_4$ (Klason, *J. pr.* [2] 33, 295).

Triphenylcyanuramide. Triphenylmelamine $C_{21}H_{18}N_6$ *i.e.*  $(CN)_3\begin{matrix}\diagup NHPh\\ -NHPh\\ \diagdown NHPh\end{matrix}$. Needles. [228°]. (360° sublimes). Insol. usual solvents. Sl. sol. glacial acetic acid (Hofmann, *B.* 18, 3218; Klason).

Pseudotriphenylcyanuramide. Triphenylmelamine $C_3H_3Ph_3N_6$. Formed by the destructive distillation of tribenzoyl-melamine. Yellow crystalline insoluble powder. Sol. hot phenol. [c. 360°] (Gerlich, *J. pr.* [2] 13, 286; Drechsel, *B.* 21, 1549).

Tetraphenylcyanuramide. Tetraphenylmelamine $C_{27}H_{22}N_6$ *i.e.*

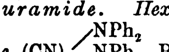


$(CN)_3\!\left\langle\begin{array}{l}NPh_2\\NPh_2\\NH_2\end{array}\right.$.

Formation.—1. By heating diphenylguanidine to 170°-180° (Hofmann, *B.* 7, 1737).—2. By the action of CNCl on aniline at 170°-180° (Weith a. Ebert, *B.* 8, 912).

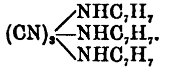
Properties.—Needles. [217°]. Insol. water; v. sl. sol. ether. Mono-acid base. Heated alone it decomposes into NH_3, mono-, and di-phenylamine and HCN; with HCl or KHO the products are CO_2, NH_3, and aniline. Hydrochloride:—B'HCl. Pt salt:—$(B'HCl)_2PtCl_4$.

Hexaphenylcyanuramide. Hexaphenylmelamine $C_{39}H_{30}N_6$ *i.e.*



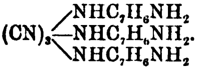
$(CN)_3\!\left\langle\begin{array}{l}NPh_2\\NPh_2\\NPh_2\end{array}\right.$. Rhombic tables (from nitrobenzene). [above 300°]. Insol. usual solvents. Does not combine with HCl. At 200° HCl decomposes it into diphenylamine and cyanuric acid (Hofmann, *B.* 18, 3219).

Tri-p-tolylcyanuramide. Tri-p-tolylmelamine $C_{24}H_{24}N_6$ *i.e.*



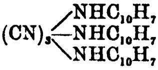
$(CN)_3\!\left\langle\begin{array}{l}NHC_7H_7\\NHC_7H_7\\NHC_7H_7\end{array}\right.$. Indifferent. Insoluble. Needles. [283°] (Klason, *J. pr.* [2] 33, 294).

Triamido-tritolyl cyanuramide. Tritoluidylmelamine $C_{24}H_{27}N_9$ *i.e.*



$(CN)_3\!\left\langle\begin{array}{l}NHC_7H_6NH_2\\NHC_7H_6NH_2\\NHC_7H_6NH_2\end{array}\right.$. Formed by the action of tolylene-diamine on cyanuric chloride (Fries, *C. J.* 49, 314 a. 739). The two intermediate compounds *mono-* and *di-tolylene-amido-cyanuric chloride* are also formed in this reaction (Fries).

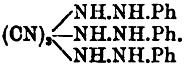
Trinaphthyl-cyanuramide. Trinaphthylmelamine $C_{33}H_{24}N_6$ *i.e.*



$(CN)_3\!\left\langle\begin{array}{l}NHC_{10}H_7\\NHC_{10}H_7\\NHC_{10}H_7\end{array}\right.$

Formed by the action of (α) and (β) naphthylamine on $(CN)_3Cl_3$ (α)-*trinaphthyl-melamine* [223°] and (β)-*trinaphthyl-melamine* [209°] together with the (α) and (β) *mono-* and *dinaphthylamido-cyanuric chlorides* are formed (Fries).

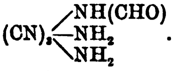
Triphenyl-tri-amido-cyanuramide. Trianilylmelamine $C_{21}H_{21}N_9$ *i.e.*



$(CN)_3\!\left\langle\begin{array}{l}NH.NH.Ph\\NH.NH.Ph\\NH.NH.Ph\end{array}\right.$. Obtained together with the *mono-* and *diphenylhydrazine-cyanuric chloride* by the action of phenylhydrazine on $(CN)_3Cl_3$ (Fries).

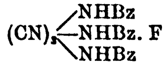
ALKOYL DERIVATIVES.

Formyl-cyanuramide. Formyl-melamine $C_4H_6N_6O$ *i.e.*



$(CN)_3\!\left\langle\begin{array}{l}NH(CHO)\\NH_2\\NH_2\end{array}\right.$. Prepared by the action of oxalic ether on cyanamide (Mulder, *B.* 7, 1631). Insol. water. Decomposed by acids or long boiling with water.

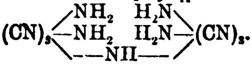
Tribenzoyl-cyanuramide. Tribenzoylmelamine $C_{24}H_{18}N_6O_3$ *i.e.*



$(CN)_3\!\left\langle\begin{array}{l}NHBz\\NHBz\\NHBz\end{array}\right.$. Formed by polymerisation of benzoyl-cyanamide. Yellow powder. [275°]. Insol. water, alcohol, and ether. Heated the products are CO_2, HCN, benzonitrile, dibenzoyldicyanamide, and pseudotriphenyl-melamine (Gerlich, *J. pr.* [2] 13, 272).

Condensed cyanuramido- compounds.

Melam $C_6H_9N_{11}$ *i.e.*

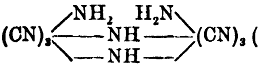


$(CN)_3\!\left\langle\begin{array}{c}NH_2\quad H_2N\\NH_2\quad H_2N\\—NH—\end{array}\right\rangle(CN)_3$.

Preparation.—Crude melam is obtained by the action of heat on ammonium thiocyanate $16CNSNH_4 = 2C_6H_9N_{11} + 5(NH_4)_2S + 4CS_2 + 3H_2S$. A strong heat should be applied, best by means of a metal bath, rising quickly to 300°, and continued till the evolution of gas ceases (Liebig, *A.* 10, 10; Claus, *A.* 179, 118). The product consists of melam thiocyanate and melem. It is washed by boiling with water and afterwards with cold dilute potash. Then it is dissolved in hot dilute HCl and reppd. by KHO (Klason, *J. pr.* [2] 33, 286).

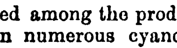
Properties.—An indifferent insoluble powder. Slightly sol. acids and hot alkalis. Heated alone it yields NH_3 and mellon; with dilute acids or alkalis it gives NH_3 and ammeline; with conc. HNO_3 cyanuric acid.

Melem $C_6H_6N_{10}$ *i.e.*



$(CN)_3\!\left\langle\begin{array}{c}NH_2\quad H_2N\\—NH—\\—NH—\end{array}\right\rangle(CN)_3$ (?). Prepared by digesting 1 pt. of crude melam with 4 pts. KHO and 80 pts. of water for 24 hrs. at 100°. Melem remains unacted upon, while melam is converted into ammeline. By heating with conc. KHO melem forms ammelide and NH_3 (Klason, *J. pr.* [2] 33, 287).

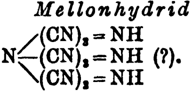
Mellon $C_6H_3N_9$ *i.e.*



$(CN)_3\!\left\langle\begin{array}{c}NH\\NH\\NH\end{array}\right\rangle(CN)_3$ (?).

This compound, which is the homologous trimolecular modification of cyanogen cyanamide (CN).NH.(CN), of which metallic derivatives are known (Bannow), is formed among the products of the action of heat on numerous cyanogen derivatives—pseudothiocyanogen, mercuric thiocyanate, ammonium thiocyanate, melem, melamine, ammeline, ammelide, diamido-cyanuric chloride, cyanamide, &c. (Liebig, *A.* 10, 4; 50, 342; Laurent a. Gerhardt, *A. Ch.* [2] 19, 85; Vœlckel, *P.* 61, 375). A light yellow powder. Insol. water, acids, and alkalis. Heated alone it breaks down into N, C_2N_2, and HCN; with KHO, into NH_3 and mellonpotassium, and with HNO_3 into cyanilic acid and NH_3.

Mellonhydride $C_9H_3N_{13}$ *i.e.*



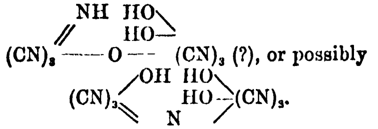
$N\!\left\langle\begin{array}{l}(CN)_3=NH\\(CN)_3=NH\\(CN)_3=NH\end{array}\right.$ (?).

Preparation.—The potassium salt of mellonhydride is formed either by heating a mixture of mellon and KHOAq in presence of cyanogen, or by melting potassium thiocyanate together with melam, mellon, or $SbCl_3$ (Liebig, *A.* 95, 271; Volhard, *J. pr.* [2] 9, 29; Klason, *J. pr.* [2] 33, 289). The potassium salt is converted into a copper compound, and this decomposed by H_2S gives an aqueous solution of the free hydride.

Properties.—A strongly acid solution. Decomposes carbonates. All attempts to isolate the free hydride have been unsuccessful. It forms primary, secondary, and tertiary salts.

Salts. – $KH_2C_9N_{13}$. – $K_2HC_9N_{13}$ 3aq. — $K_3C_9N_{13}$ 5aq. Needles. Bitter. S. 2·7 in cold water. – $Ca_3(C_9N_{13})_2$ 4aq. — $Ba_3(C_9N_{13})_2$ 6aq. — $Cu_3(C_9N_{13})_2$ 5aq.—$Ag_3C_9N_{13}$.

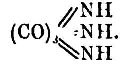
Cyameluric acid $C_6H_3N_7O_3 2\frac{1}{2}H_2O$ *i.e.*



Formation.– By the long-continued digestion of potassium mellon with KHO and liberation of the free acid from the salt so obtained by HCl (Henneberg, *A.* 73, 235; Volhard, *J. pr.* [2] 9, 30).

Properties.—Powerful tribasic acid. White powder. V. sl. sol. water. Heated alone it yields cyanic and cyanuric acids and mellon.

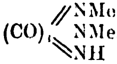
Salts.– K_3A''' 3aq: needles. Sol. water with strong alkaline reaction (Liebig, *A.* 95, 281).– KH_2A''' 2aq.—$Ba_3A'''_2$ aq.–Ag_3A'''.

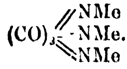
Isocyanuric acid  $(CO)_3\begin{cases}=NH\\=NH\\=NH\end{cases}$. The hypothetical acid corresponding to the isocyanuric ethers.

ALKYL DERIVATIVES.

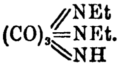
Formation. 1. By the distillation of a mixture of potassium cyanurate and alkyl sodium sulphate (Wurtz, *A. Ch.* [3] 42, 57). –2. By the action of heat on alkylacetylurea alkyl isocyanurates are formed, together with acetamide and other products (Hofmann, *B.* 14, 2728).—3. From dialkylureas by heating (Wurtz, *J.* 1856, 700).– 4. By the action of alkyl iodides on silver or potassium cyanurate (Habich a. Limpricht, *A.* 109, 112; Ponomareff, *B.* 18, 3270).– 5. By polymerisation of isocyanic ethers or the intramolecular change of normal cyanuric ethers (Hofmann a. Olshausen, *B.* 3, 271).

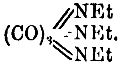
Reactions.—1. The action of *water* (heating with dilute acids) causes the isocyanuric ethers to break down like the isocyanic ethers into CO_2 and amines (Wurtz). 2. With PCl_5 isocyanuric ethers do not give cyanuric chloride, but chloroalkyl substitution compounds (Hofmann, *B.* 18, 2800).

Dimethylisocyanuric acid $C_5H_7N_3O_3$ *i.e.*  $(CO)_3\begin{cases}=NMe\\=NMe\\=NH\end{cases}$. Needles. Crystal measurements (Hofmann, *B.* 19, 2071). [222°]. Its salts are not very stable. Ammoniacal solution gives with $CuSO_4$ a violet Cu salt. Silver salt v. sl. sol. water (Hofmann, *B.* 14, 2728; 19, 2069)

Trimethylisocyanurate $C_6H_9N_3O_3$ *i.e.*  $(CO)_3\begin{cases}=NMe\\=NMe\\=NMe\end{cases}$. Prisms. Crystals measured (Hofmann, *B.* 19, 2067). [175°–176°]. (274°). Insol. cold, sl. sol. hot water. Sol. alcohol. Treated with PCl_5 the compound $(CN)_3(OCH_2Cl)_3$ is formed.—$B'HgCl_2$ crystals (Wurtz; Hofmann a. Olshausen; Ponomareff, *B.* 18, 3271; Hofmann, *B.* 18, 2800; 19, 2093).

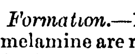
Combinations with formamide (Gautier, *A.* 149, 313) $(CN)_3(NMe)_3,HCONH_2$. Obtained by the oxidation of acetonitrile. [175° with partial sublimation] $(CN)_3(NMe)_3,(HCO)_2NH$. [163°]. (168°).

Diethylisocyanuric acid $C_7H_{11}N_3O_3$ *i.e.*  $(CO)_3\begin{cases}=NEt\\=NEt\\=NH\end{cases}$. Hexagonal prisms. Measurements (Hofmann, *B.* 19, 2078). [173°]. Sl. sol. cold, sol. hot, water. Sol. alcohol, ether, ammonia, and alkalis. — B'_2Ba aq: sol. water. — $B'Ag$: needles, ppd. by ammoniacal $AgNO_3$. Copper salt rose-coloured (Habich a. Limpricht, *A.* 109, 112; Wurtz, *J.* 1856, 700; Ponomareff, *B.* 18, 3270).

Triethyl-isocyanurate $C_9H_{15}N_3O_3$ *i.e.*  $(CO)_3\begin{cases}=NEt\\=NEt\\=NEt\end{cases}$. Rhombic prisms (Hofmann, *B.* 19 2076). [95°]. (276°). Distils with steam. Sol. hot water, alcohol, and acids. PCl_5 has no action, and KHO decomposes the ether with difficulty. Heated with $Ba(OH)_2Aq$ it yields CO_2 and triethylbiuret, and similarly with sodium alcoholate ethylene, ethylamine, triethylguanidine, and triethylbiuret are formed (Hofmann, *J.* 1861, 516). Chlorine forms substitution derivatives (Wurtz; Habich a. Limpricht; Ponomareff; Gal, *A.* 137, 127).

Tetrachlorotriethyl isocyanurate $C_9H_{11}Cl_4N_3O_3$. Crystals. Insol. water; sol. alcohol. Not ppd. by $AgNO_3$. Compounds containing less Cl are obtained by the action of alcoholic potash (Habich a. Limpricht, *A.* 109, 109).

Tribenzyl isocyanurate v. BENZYL-CYANURATE.

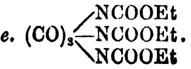
Triphenyl isocyanurate $C_{21}H_{15}N_3O_3$ *i.e.*  $(CO)_3\begin{cases}=NPh\\=NPh\\=NPh\end{cases}$.

Formation.—1. The NH groups of triphenylisomelamine are replaced by oxygen by treatment with alcohol and HCl.—2. Phenyl isocyanate is polymerised to isocyanurate by heating for 3 hrs. at 100° with dry potassium acetate (Hofmann, *B.* 3, 268; 18, 765 a. 3225).

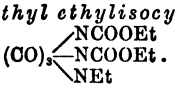
Properties.—Prisms. [274°–275°]. Distils mostly unchanged. Insol. water; sol. hot alcohol.

CARBOXYLIC DERIVATIVES.

By the action of ethyl chloroformate ClCOOEt on potassium cyanate, besides carboxethyl-carbamic ether, three carboxethyl derivatives of isocyanuric acid have been obtained. These are triethyl isocyanurcarboxylate, and two derivatives intermediate between that compound and isocyanuric ether. By distillation they lose CO_2 and are converted into isocyanurates (Wurtz a. Henninger, *Bl.* 44, 26).

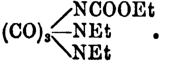
Triethyl isocyanurcarboxylate $C_{12}H_{15}N_3O_9$ *i.e.*  $(CO)_3\begin{cases}-NCOOEt\\-NCOOEt\\-NCOOEt\end{cases}$. Crystals. [118°–119°].

Dicarboxethyl ethylisocyanurate $C_{11}H_{15}N_3O_7$ i.e.



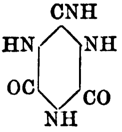
$(CO)_3{<}\begin{matrix}NCOOEt\\NCOOEt\\NEt\end{matrix}$. Crystals. [123°].

Carboxethyl diethylisocyanurate $C_{10}H_{15}N_3O_5$ i.e.



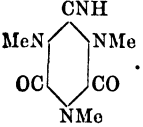
$(CO)_3{<}\begin{matrix}NCOOEt\\NEt\\NEt\end{matrix}$. Needles. [107°].

Isoammelide (hypothetical)



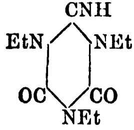
ALKYL DERIVATIVES.

Trimethylisoammelide $C_6H_{10}N_4O_2$ i.e.



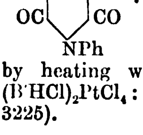
Formed by the action of HCl on the platinum salt of trimethylisomelamine.—B'HCl: needles; sol. alcohol, insol. ether.—B'HCl,$AuCl_3$: needles; v. sl. sol. water (Hofmann, *B.* 18, 2786).

Triethylisoammelide $C_9H_{16}N_4O_2$ i.e.



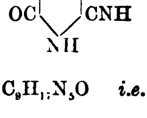
Obtained by treatment of triethyl isomelamine with HCl. — $(B'HCl)_2PtCl_4$ (Hofmann, *B.* 18, 2789).

Triphenylisoammelide $C_{21}H_{16}N_4O_2$ i.e.



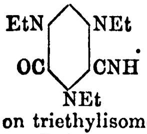
From triphenyl isomelamine by heating with HCl. Needles. [272°].—$(B'HCl)_2PtCl_4$: amorphous (Hofmann, *B.* 18, 3225).

Isoammeline (hypothetical)



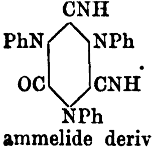
ALKYL DERIVATIVES.

Triethylisoammeline $C_9H_{17}N_5O$ i.e.



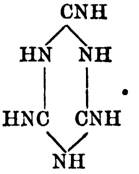
Formed by the action of HCl on triethylisomelamine (Hofmann, *B.* 18, 2789).

Triphenylisoammeline $C_{21}H_{17}N_5O$ i.e.



This and the corresponding isoammelide derivative represent the two possible intermediate compounds between alkylisomelamine and alkyliso-cyanurate. Both are prepared by treatment of triphenylisomelamine with HCl, the isoammeline being first formed (Hofmann, *B.* 18, 3224).

Isomelamine (hypothetical) $(CNH)_3 3NH$ i.e.



ALKYL DERIVATIVES.

Formation.—By heating solutions of alkylcyanamides, whereby polymerisation takes place (Hofmann, *B.* 2, 602).

Reactions.—Heated with dilute acids the alkyl isomelamines yield NH_3, and become converted into isocyanurates (Hofmann).

Trimethyl isomelamine $C_6H_{12}N_6$ 3aq i.e. $(CNMe)_3(NH)_3$ 3aq. Needles. [179°]. Commences to sublime above 100°. Sol. water and alcohol, insol. ether. Reaction alkaline. HCl acts in the first instance, forming trimethylisoammelide and then trimethylisocyanurate. — $B''(HCl)_2,PtCl_4$. Laminæ. V. sl. sol. water and alcohol.—$B''(HCl)_2,AuCl_4$. Needles (Hofmann, *B.* 3, 264; 18, 2784; Baumann, *B.* 6, 1372).

Triethylisomelamine $C_9H_{18}N_6$ 4aq i.e. $(CNEt)_3(NH)_3$ 4aq. Crystals. [92°]. V. sol. water and alcohol. Reaction alkaline. HCl reacts forming successively triethyl-isoammeline, triethyl-isoammelide, and triethyl isocyanurate.—*Salts*: $B''(HCl)_2,PtCl_4$. Sol. water. — $B'(HClAuCl_3)_2$. Needles. Sl. sol. water and alcohol (Hofmann, *B.* 2, 602; 3, 266; 18, 2788).

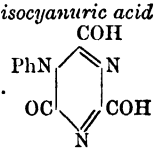
Tribenzyl-isomelamine $C_{24}H_{24}N_6$ i.e. $(CNC_7H_7)_3(NH)_3$. Laminæ [higher than benzyl-cyanamide].—$B''(HCl)_2$. Needles. Sl. sol. water (Strakosch, *B.* 5, 694).

Triphenyl-isomelamine $C_{21}H_{18}N_6$ i.e. $(CNPh)_3 3NH$. Needles. [185°]. V. sl. sol. hot water, sol. alcohol and ether. HCl reacts forming successively triphenyl-isoammeline, triphenyl-isoammelide, and triphenyl-isocyanurate.—$B_3(HCl)_2PtCl_4$. Needles (Hofmann, *B.* 3, 267; 18, 3223).

Normal-iso Cyanuric acids (hypothetical).

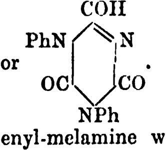
ALKYL DERIVATIVES.

Phenyliso-dinormal cyanuric acid. Monophenyl isocyanuric acid $C_9H_7N_3O_3$ i.e.



Formed by the action of conc. HCl on Rathke's triphenyl-ammeline. Flat needles. [285°-289°]. V. sol. hot, v. sl. sol. cold water (Rathke, *B.* 20, 1070, 21, 868).

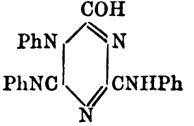
Diphenyliso-normal cyanuric acid $C_{15}H_{11}N_3O_3$ or

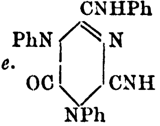


Prepared by heating *u*-triphenyl-melamine with conc. HCl at 150°. The phenylamido group is thus replaced by hydroxyl and the imido- groups by oxygen. Needles or laminæ. [261°]. Insol. water, sol. alcohol, v. sl. sol. ether. With conc. HCl at 280° it breaks down into CO_2, NH_3, and aniline. $C_{15}H_{10}AgN_3O_3$ crystalline pp. formed on addition of $AgNO_3$ to a solution of the sodium salt (Hofmann, *B.* 18, 3230).

Normal-iso ammelines (hypothetical).

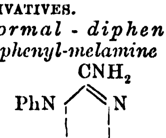
ALKYL DERIVATIVES.

Phenylnormalamido-diphenyliso-amido-cyanuric acid. Triphenyl ammeline $C_{21}H_{17}N_5O$ *i.e.* . Obtained by treatment of ethyltriphenylthioammeline hydrobromide, a compound prepared by the action of ethyl bromide on triphenyl-thioammeline, with alcoholic potash. Colourless laminæ. [275°]. V. sl. sol. alcohol, sl. sol. chloroform. Conc. HCl at 160° converts it into phenyliso-dinormal-cyanuric acid (Rathke, *B.* 20, 1069; 21, 868).

Phenylnormalamido-phenyliso-amido-phenylisocyanurate. Triphenyl-ammeline $C_{21}H_{17}N_5O$ *i.e.* . Prepared by acting on Hofmann's *u*-triphenylmelamine with HCl at 100°. Crystals. [265°]. Heated further with HCl it is converted into diphenyl iso-normal-cyanuric acid (Hofmann, *B.* 18, 3229).

Normal-iso melamines (hypothetical).

ALKYL DERIVATIVES.

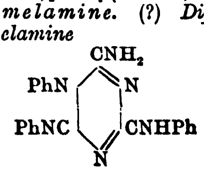
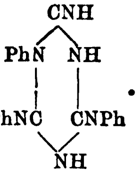
Phenylnormal-diphenyliso-melamine. u-Triphenyl-melamine $C_{21}H_{18}N_6$ *i.e.* .

Formation. — By the desulphurisation of monophenylthiourea by HgO in alcoholic solution.

Properties.—Needles. [217°]. Insol. water, sl. sol. ether. sol. chloroform, sol. dilute acids and reprecipitated by alkalis.

Reactions.—By the action of HCl it is converted at 100° into Hofmann's isonormal triphenylammeline, and at 150°-200° into diphenylisonormal cyanuric acid (Hofmann, *B.* 18, 3226).

Diphenyl-melamine $C_{15}H_{14}N_6$. A by-product in the preparation of Rathke's triphenylmelamine. Formed together with aniline when in that process the further action of alcoholic ammonia causes the isonormal triphenylmelamine to change into the normal isomeride. It may possibly prove to be a normal compound. [202°-204°]. $(B'HCl)_2PtCl_4$ (Rathke, *B.* 21, 872).

Triphenylmelamine. (?) *Diphenylnormal phenylisomelamine* $C_{21}H_{18}N_6$ *i.e.* (?)  or .

Formation.—By the action of alcoholic ammonia on ethyl triphenyl-thio-ammeline hydrobromide, the reaction being: $C_3N_5HPh_3SEt + NH_3 = C_3N_5HPh_3NH_2 + EtSH$. Diphenylammeline, aniline, and normal triphenylmelamine are formed in the same reaction (Rathke, *B.* 20, 1071; 21, 868).

Properties.—Prisms. [221°]. Sol. hot alcohol. Base. The hydrochloride and sulphate are soluble, the nitrate is sl. sol. water.

Reactions.—1. Heated with alcohol and ammonia it changes to normal triphenylmelamine. 2. Heated with conc. HCl at 125° it is converted into Rathke's triphenylammeline, and at higher temperatures into phenyl iso-dinormal-cyanuric acid.

Other isomerides of cyanuric acid.

The members of this division of trimolecular compounds are so little known that it would be premature to attempt to assign to them structural formulæ.

The (α) and (β) *Cyanuric acids* (Herzig, *B.* 12, 170) are not included, recent investigation having shown that when purified they are in all respects identical with each other and with ordinary cyanuric acid (Senier, *C. J.* 49, 693 a. 743).

Cyamelide $(CNOH)_x$.

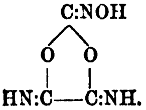
Formation.—1. Liquid cyanic acid polymerises slowly at 0°, and instantly at higher temperatures with evolution of heat forming cyamelide. This reaction takes place when cyanates are treated with anhydrous acids (Liebig a. Wöhler, *P.* 15, 561; 20, 384; Troost a. Hautefeuille, *J.* 1869, 99; Weltzien, *A.* 132, 222).—2. Is formed, together with cyanuric acid, by the action of $(CN)_3Cl_3$ on water (Liebig, *P.* 15, 563). *Cf.* Mulder (*R.* 6, 199).

Properties.—Tasteless, inodorous solid. Insol. water, alcohol, ether, and dilute acid, sol. KHOAq or NH_4HOAq, cyanurate being formed on evaporation. Heated alone it evolves cyanic acid. Heated with H_2SO_4 it is converted into ordinary cyanuric acid. Cyamelide may possibly prove to be free isocyanuric acid (Klason, *J. pr.* [2] 33, 129).

Cyanilic acid $C_3N_3O_3H_32H_2O$.

This compound is so nearly related to cyanuric acid that when further studied it may prove to be identical with it. Mellon is heated together with HNO_3, and the product extracted with water. Recrystallised from water it consists of pearly laminæ, or from HNO_3 of four-sided prisms. By solution in H_2SO_4 it is converted into cyanuric acid, which falls on the addition of water. It has the same proportion of water of crystallisation, and the crystals effloresce just in the same manner as cyanuric acid. With $AgNO_3$ it forms a salt $AgH_2C_2H_3O_2$, corresponding to a similar cyanurate. Its solubility in water was, however, found to be greater than that of cyanuric acid, and its crystalline form to be different (Liebig, *A.* 10, 34).

Fulminuric acid $HC_3H_2N_3O_3$ *i.e.*



Formation.—By heating fulminating mercury (not fulminating silver) with an aqueous solution of alkaline chlorides or iodides (Liebig, *A.* 95, 282; Schischkow, *A.* 97, 53; 101, 213), or with water (Ehrenberg, *J. pr.* [2] 32, 98), or in tubes with alcoholic ammonia (Steiner, *B.* 9, 781). The potassium or ammonium salt thus obtained is converted into the lead or silver compound which suspended in water is treated with H_2S. The aqueous solution which results deposits the free fulminuric acid as an indistinct crystalline powder on spontaneous evaporation.

Properties. — Small anhydrous colourless prisms, from alcohol. Sol. water, alcohol, and ether. Solutions have an acid reaction, and give a characteristic deep blue pp. with ammonio copper sulphate.

Reactions.—1. Heated it explodes at 145°.—2. Heated with dilute acids or alkalis NH_3, CO_2 and $H_2C_2O_4$ are formed (Steiner, *B.* 5, 381). 3. The silver salt heated with conc. HCl separates one of its N atoms as NH_2OH (Ehrenberg). 4. Two atoms of N are evolved as ammonia by heating with soda lime.—5. With chloride of lime it forms $C(NO_2)Cl_3$.—6. With H_2SO_4 nitroacetonitrile is formed, and in presence of HNO_3 tri-nitroacetonitrile.

Halogen derivatives.—**Chlorofulminuric acid** $C_3H_2ClN_3O_3$. Salts $AgC_3HClN_3O_3$. — $Ag_2C_3ClN_3O_3$. **Bromofulminuric acid** $C_3H_2BrN_3O_3$ (Ehrenberg, *J. pr.* [2] 32, 111).

Metallic derivatives.—NH_4A': prisms, sol. water, insol. alcohol (Liebig). $(NH_4A')_2(Hg2SCN)_3$ [150°] (Ehrenberg, *J. pr.* [2] 30, 64). — $NH_4A',HgSCN$ [161°]. — $(NH_4A')_32Hg(SCN)_2$ [156°]. — KA': prisms, sol. water, insol. alcohol. Explodes at 225° (Schischkow).—$MgA'_2,5aq$: needles (Steiner).—BaA'_22aq: prisms (Liebig).—$ZnA'_2,5aq$: needles (Steiner) — HgA'_2: crystalline powder (Steiner).—HgA'_2,HgO (Steiner). — PbA'_2, 2aq: needles (Steiner). — CuA'_2, 4aq: emerald green rhombs. $CuA'_2,4NH_3$: characteristic deep blue pp. Prisms. Insol. water, v. sl. sol. ammonia.—AgA' (Liebig).

Alkyl derivatives.—An unstable oil $C_6H_{11}NO_5$ is obtained by passing HCl into a mixture of potassium fulminurate and alcohol. It combines with NH_3 and amines—$C_6H_{11}NO_5,NH_3$ [152°]. $C_6H_{11}NO_5,NH_2Ph$: needles. [81°] (Ehrenberg, *J. pr.* [2] 32, 106; Schischkow, *A.* 97, 61).

Isofulminuric acid $C_3H_3N_3O_3$.

Formation.—Together with other products by the action of aqueous ammonia on an ethereal solution of fulminic acid obtained by leading HCl at 0° into a mixture of fulminating mercury and ether. The aqueous solution on spontaneous evaporation deposits fulminuramide, and from the solution by further treatment isofulminuric acid is obtained.

Properties.—Pulverulent. Chars without melting when heated. V. sol. water and alcohol. Gives no pp with ammonio-cupric sulphate.

Salts.—NH_4A'.—BaA'_2.—AgA': amorphous pp., insol. cold water (Ehrenberg, *J. pr.* [2] 30, 48).

Fulminuramide.—$C_3H_2NH_2N_3O_2$: long minute needles.—$(B')_2CuO2NH_3$: light blue pp.—$B'_2,AgNO_3$: needles (Ehrenberg).

Metafulminuric acid $C_3H_3N_3O_3,3H_2O$.

Formation.—By the action of dilute H_2SO_4 on sodium fulminate. The product is extracted with ether which evaporated in a current of air below 30° deposits the metafulminuric acid in needles. The solution contains isocyanilic acid which is formed in the same reaction.

Properties.—[81°]. Anhydrous acid explodes at 106°. Tribasic acid. V. sol. alcohol and benzene, less so in water and ether. Decomposes gradually with evolution of HCN.

Reactions.—1. KHO or water at 130° breaks it down into CO_2 and NH_3.—2. Heated with conc. HCl, NH_2OH is formed.—3. Gradually changes into (β)-isofulminuric acid on standing.

Salts.—NH_4H_2A'''.—$(NH_4)_2HA'''$.—$H_3A'''(NH_2Me)_2$: yellow needles. — K_3A'''. — $PbHA'''aq$: lemon-yellow insol. pp.—$Ag_2HA'''aq$. On adding $AgNO_3$ to the aqueous solution the silver salt falls as a characteristic cinnabar red, at first gelatinous, precipitate. Explodes when dry at 86° (Scholvien, *J. pr.* [2] 32, 464).

(β)-***Isofulminuric acid*** $C_3H_3N_3O_32\frac{1}{2}H_2O$. Metafulminuric acid changes gradually on standing, being converted into this metameric modification. Needles, from water. [188°]. [196° anhydrous, with decomposition]. Sol. water and alcohol.

Salts.—NH_4A'.—BaA'_2.—AgA' insol. pp., crystallises in needles (Scholvien, *J. pr.* [2] 32, 474).

Isocyanilic acid $(CNOH)_3$.

Formation.—To the ethereal mother-liquor from which metafulminuric acid has been separated, water is added and the evaporation continued, when isocyanilic acid comes out in needles. It may be recrystallised from water.

Properties.—Does not explode on heating. Sol. hot water, alcohol, and ether. Gives no pp. in aqueous solution on adding $AgNO_3$ or $Pb(C_2H_3O_2)_2$ or $CuSO_4$. Heated with conc. KHO the solution is coloured deep red violet, and on the addition of alcohol a salt of the same colour is ppd. This red violet compound in aqueous solution gives with $Pb(C_2H_3O_2)_2$ a bright red violet explosive lead salt $Pb_5C_5H_4N_4O_8$ (Scholvien, *J. pr.* [2] 32, 476).

A. S.

CYANIDES (including SULPHOCYANIDES and SELENOCYANIDES). *Binary compounds of cyanogen.* In this article only metallic cyanides are described. Alkyl cyanides are described as *nitriles*; *e.g.* for description of $CH_3.CN$ *v.* ACETONITRILE.

Cyanogen forms binary compounds with above 30 metals; most of these cyanides form several, some form very many, double cyanides; some of the double cyanides are best regarded as metallic derivatives of acids composed of H combined with metals and the atomic group CN (*v. post*). Cyanogen also forms binary compounds with the non-metals Br, Cl, I, P, Se, and S. Of these compounds, CNBr, CNCl, and CNI are described under CYANIC ACID (p. 312, 313); the others are described under CYANOGEN as *Cyanogen phosphide*, &c.

The simple cyanides may be regarded as derived from cyanhydric acid NCH, by replacing H by metals; the general formulæ expressing their compositions are NC.M, $(NC)_2M^{II}$, $(NC)_3M^{III}$, &c.

Alkali cyanides are formed by the direct union of cyanogen with alkali metals, by reactions between HCNAq and alkali oxides, by strongly heating nitrogenous organic matter with alkali carbonate. Many other cyanides are obtainable from alkali cyanides by double decomposition.

Alkali and alkaline earth cyanides are soluble in water; the other simple cyanides, with the exception of $HgCy_2$, are insoluble in water, but may dissolve in solutions of alkali cyanides with production of double cyanides.

Alkali cyanides are very easily decomposed with evolution of HCN, passage of a current of air free from CO_2 suffices to effect this change. Some of the insoluble cyanides are readily decomposed by dilute acids, *e.g.* $PbCy_2$ and $ZnCy_2$; others are very stable towards acids, *e.g.* cyanides of Au, Hg, and Ag. Hot conc. H_2SO_4 decomposes all cyanides, some easily, others slowly; the products are sulphate and HCN or CO and NH_3. Alkali cyanides are unchanged by heat alone; cyanides of the heavy metals are decomposed by heat, generally forming metal and Cy, sometimes N is evolved and C deposited on the metal, or a carbide of the metal is formed. Water decomposes cyanides at high temperatures (250°–300°), giving $(NH_4)_2CO_3$ and $HCO_2.NH_4$ with metallic oxide, or sometimes metal and $(NH_4)_2CO_3$. Chlorine decomposes most cyanides generally forming metallic chloride and CyCl. Boiling with water and excess of HgO decomposes all cyanides, except platino-cyanides, with formation of $HgCy_2$ and oxide of the metal of the cyanide.

Many cyanides form double salts, generally with haloid metallic compounds.

Very many cyanides combine with other cyanides to form double cyanides. These double cyanides are divisible into two classes, according as they are, or are not, decomposed by solutions of mineral acids with evolution of HCN. Silver potassium cyanide, $AgKCy_2$, for instance, reacts with dilute HNO_3Aq to give AgCy, KNO_3, and HCN, and with dilute HClAq it gives AgCl, KCl, and HCN; potassium ferrocyanide, K_4FeCy_6, on the other hand, reacts with HClAq to give ferrocyanic acid H_4FeCy_6. The members of the second class of double cyanides are generally regarded as metallic derivatives of acids which are themselves composed of H united with a metal and the radicle cyanogen, the metal and cyanogen together forming the negative radicle of the acid; thus, *ferrocyanic acid* H_4FeCy_6 (better called *ferrocyanhydric acid*) forms a series of well-marked stable metallic derivatives which are obtainable from the acid by reactions similar to those whereby salts are produced from HNO_3, H_2SO_4, H_3PO_4, &c.

Manganocyanic acid (or manganocyanhydric acid) H_4MnCy_6, *cobalticyanic acid* (or cobalticyanhydric acid) H_3CoCy_6, *auricyanic acid* (or auricyanhydric acid) $HAuCy_4$, *platincyanic acid* (or platincyanhydric acid) H_2PtCy_4, and some other acids the negative radicles of which are composed of metal combined with cyanogen, have been isolated. Some of these metallic-cyanogen acids form derivatives in which part of the negative radicle is replaced by a negative group, *e.g.* H_2FeCy_5NO. A few metallic-halogen acids are known, more or less analogous to the metallic-cyanogen acids, *e.g.* $H.AuCl_4$, $H_2.HgCl_4$, $H_2.PtCl_6$; but the metallic-cyanogen acids are more numerous, and form many more stable salts, than the metallic-halogen acids. The negative character of the radicle CN is well seen in the production of the numerous ferrocyanides, manganocyanides, platinocyanides, &c. The affinities of a few metallic-cyanogen acids have been determined (*v.*, *e.g.*, p. 333); they seem to be very strong acids; on the other hand cyanhydric acid N.CH is an extremely weak acid (*v.* CYANHYDRIC ACID, p. 301); but sulphocyanic acid, N.CSH, has a very large affinity (*v.* SULPHOCYANIC ACID, p. 303).

It would be possible, and for some reasons advantageous, to divide the metallic cyanides into two main classes; class I. would include those cyanides which are decomposed by dilute mineral acids with evolution of HCN, and are therefore to be regarded as derivatives of HCN, and also those which although not yielding HCN by reactions with dilute acids must nevertheless, on account of their composition and modes of preparation, be regarded as derived from HCN (*e.g.* $HgCy_2$); class II. would include those cyanides which yield metallic-cyanogen acids or are derived from such acids. The first class would contain all the simple, and many double, cyanides. Some double cyanides would hardly fall into either class; $HgCy_2.2KCy$ for instance reacts with solutions of salts of Zn, Cd, Pb, &c., to form salts of the general form $HgCy_2.MCy_2$ (M = Zn, Pb, Cd, &c.), hence $HgCy_2.2KCy$ seems to be the K salt of the hypothetical acid H_2HgCy_4. The metallic-cyanogen acids which have been isolated are H_4CrCy_6 (salts of H_3CrCy_6 are also known), H_4CoCy_6, H_3CoCy_6, $HAuCy_4$, H_3IrCy_6, H_4FeCy_6, H_3FeCy_6, H_4MnCy_6, H_4OsCy_6, salts of H_2PtCy_4, $H_2PtCy_4Cl_2$ (or Br_2), salts of H_3RhCy_6, H_4RuCy_6; salts of the hypothetical H_2PdCy_4 are also known, but they react more like double cyanides. No nickelo- or nickeli-cyanides are known corresponding to M_3CoCy_6 and M_4CoCy_6; Ni double cyanides are easily decomposed by dilute acids with evolution of HCy, and are therefore to be classed with the less stable double cyanides.

Those cyanides, simple or double, which are readily decomposed by dilute acids with formation of HCy are poisonous; the stable salts of metallic-cyanogen acids, *e.g.* K_4FeCy_6, are not poisonous.

In this article the cyanides will be described in alphabetical order; the descriptions of the various compounds will show to which of the two main classes of cyanides they belong.

This article also includes descriptions of the *sulphocyanides* and the *selenocyanides*.

SELENOCYANIDES. These compounds are derived from *selenocyanhydric acid* HSeCN. The acid itself is only known in aqueous solution; it is very easily decomposed to HCN and Se; the K salt is obtained by dissolving Se in KCNAq. (For individual selenocyanides, *v.* p. 348).

SULPHOCYANIDES *Metallic derivatives of sulphocyanic* (or thiocyanic) *acid*. Sulphocyanic acid almost certainly has the constitution HS.CN; while the replaceable H of cyanic acid is probably in direct union with N. The metallic sulphocyanides are not strictly comparable with the metallic cyanates; for this reason it seems better to use the name *sulphocyanides* rather than *sulpho-* (or thio-) *cyanates*. Cyanhydric acid is an extremely weak acid, but the affinity of sulphocyanic acid is nearly equal to that of hydrochloric (*v.* Ostwald's *Lehrbuch der allgemeinen Chemie*, 2, 849).

The general formulæ expressing the composition of sulphocyanides are NCS.M, $(NCS)_2M^{II}$, $(NCS)_3M^{III}$, &c. These salts are sometimes called *rhodanides*, a name first given to them by Berzelius because of the red colour which they give with ferric salts (ῥόδον).

Sulphocyanide of K is formed by direct addition of S to KCN; Na SCN is produced by passing CS_2 over heated $NaNH_2$ ($NaNH_2 + CS_2 = NCS.Na + H_2S$); $NH_4.SCN$ may be obtained by adding $(NH_4)_2S_2$ to NCHAq, or by heating CS_2 with alcoholic NH_3 ($CS_2 + 4NH_3 = NCS.NH_4 + (NH_4)_2S$); the sulphocyanides of the heavy metals are usually formed by double decomposition from the alkali sulphocyanides.

Most sulphocyanides are soluble in water; the salts of Cu, Pb, Hg, and Ag are insoluble. Dry alkali sulphocyanides may be heated in absence of air without change; in presence of air SO_2 is evolved and sulphate and cyanate are produced. Sulphocyanides of the heavy metals are decomposed by heat, generally giving S, CS_2, metallic sulphide, and *mellon* (*q. v.* p. 323), on strongly heating the mellon yields Cy and N. The insoluble sulphocyanides are completely decomposed by H_2S. Sulphocyanides of P and Si, $P(SCy)_3$, and $Si(SCy)_4$ respectively, are described under PHOSPHORUS and SILICON.

Many double sulphocyanides are known; most of these react as double salts, but some as metallic derivatives of acids composed of H united with a negative radicle which is itself composed of metal and sulphocyanogen (SCN). For instance *chromsulphocyanic* (or chromsulphocyanhydric) *acid* $H_3Cr(SCN)_6$ is known in aqueous solution, and many salts of this acid have been isolated. The acid $H_2Pt(SCN)_6$ is also known in aqueous solution. (For individual sulphocyanides *v.* p. 348 *et seq.*)

Analysis of cyanides and sulphocyanides.

I. Alkali cyanides are estimated by ppn. with $AgNO_3Aq$, or by Liebig's volumetric method (*v.* CYANHYDRIC ACID).

II. Many cyanides, including the double compounds of NCK with $CuCy_2$, $NiCy_2$, and $ZnCy_2$, may be estimated by heating for some time with $AgNO_3$, then adding HNO_3Aq, and heating again; the AgCN formed is collected and weighed. According to Weith (*Fr.* 9, 379) K_4FeCy_6, K_3CoCy_6, and Prussian blue, may be wholly decomposed by heating for several hours in a closed tube with ammoniacal $AgNO_3$; oxide of the heavy metal is ppd. while NH_4Cy goes into solution; filtering and adding HNO_3Aq ppts. AgCy.

III. Mercuric cyanide may be analysed by heating with ammoniacal $Zn(NO_3)_2$, whereby $ZnCy_2$ is formed (*v.* Rose a. Finkener, *Fr.* 1, 288).

IV. Many cyanides may be analysed by long boiling with HgO and water, filtering and determining Cy by boiling with ammoniacal $Zn(NO_3)_2$.

V. The metal in most cyanides may be determined by continued heating with conc. H_2SO_4, vapourising excess of acid, and estimating the metal in the remaining sulphate by one of the usual methods.

VI. Soluble sulphocyanides may be analysed volumetrically by means of standard Ag solution in the same way as chlorides (Volhard, *Fr.* 1874 212).

CYANIDES.

Aluminium cyanide. Not isolated. A double Al-Fe cyanide is described by Tissier (*J. Ph.* 35, 88) as obtained by boiling K_4FeCy_6Aq with excess of an acid solution of a salt of Al; the composition of the pp. is approximately $3FeCy_2.2Al_2Cl_6$.

Ammonium cyanide $NH_4.CN$. Formed by passing NH_3 over red-hot coal (Kuhlman, *A.* 38, 62; Clouet, *A. Ch.* 11, 30; Langlois, *A.* 38, 64); also by passing CO and NH_3 over heated Pt black (K., *l.c.*). Prepared by heating together 3 parts dry K_4FeCy_6 with 2 parts NH_4Cl at 100° and leading the vapour into a well-cooled receiver (Bineau, *A. Ch.* 70, 263). Crystallises in cubes; volatilises at c. 36° with dissociation into $HCN + NH_3$ (Bineau, *l. c.*; Deville a. Troost, *C. R.* 56, 891). Vapour is inflammable in the air. Very poisonous. Easily decomposes in the air to a brownish mass. Easily soluble in water and alcohol. Berthelot (*C. R.* 91, 82) gives the following thermal data:— $[C, N^2, H^4] = 3,200$ (formation of solid $NH_4.CN$); $[N, CN, H^4] = 40,500$ (solid $NH_4.CN$); $[HCN, NH^3]$ 20,500 (solid $NH_4.CN$ from gaseous materials); $[HCNAq, NH^3Aq] = 1,300$; $[NH^4.CN, Aq] = -4,100$

Barium cyanide $Ba(CN)_2$. Prepared by heating $Ba_2Fe(CN)_6$, and extracting with water (Schulz, *J. pr.* 68, 257). The hydrate $Ba(CN)_2.H_2O$ may be prepared by bringing HCN gas into contact with hydrated BaO (for details *v.* Joannis, *A. Ch.* [5] 27, 189). It is also formed when air is passed over a red-hot mixture of BaO and C (Margueritte a. Sourdeval, *C. R.* 50, 1100). Crystalline; quickly absorbs CO_2 from air; sl. sol. in water; heated to 300° in steam evolves NH_3. When HCN is passed into BaO in $CH_3.OH$, a crystalline powder is formed of the composition $Ba.CN.OCH_3 + CH_3.OH$, and when this is strongly heated *barium oxycyanide* $BaCy_2.BaO$ is formed (Drechsel a. Kruger, *J. pr.* [2] 21, 77). Joannis (*l.c.*) gives the following thermal data:— $[BaOAq, 2HCNAq] = 6,340$; $[BaCy^2, Aq] = 1,780$. Weselsky (*Z.* [2] 7, 61) prepares various **double cyanides containing barium cyanide** by passing HCy gas into a mixture of $BaCO_3$ with a salt of the other metal; *e.g.* using $PtCl_2Aq$ and $BaCO_3$, the double cyanide $BaCy_2.PtCy_2$ is obtained. The following double cyanides were produced: $[M = BaCy_2]$ $2M.3CdCy_2.10H_2O$; $M.Cu_2Cy_2.H_2O$; $M.NiCy_2.3H_2O$; $M.PdCy_2.4H_2O$; $M.2AgCy.H_2O$; $M.ZnCy_2.2H_2O$.

Cadmium cyanide $CdCy_2$. Obtained by dissolving freshly ppd. $CdO.M_2O$ in HCyAq, filtering from oxycyanide, and crystallising (Rammelsberg, *P.* 38, 364). Small white crystals; unchanged in air; decomposes above 200° in air. S. c. 1·7 in cold water. H.F. $[Cd, Cy^2, Aq] = 33,960$; $[CdO^2H^2, 2HCyAq] = 13,700$ (*Th.* 3, 474).

Cadmium oxycyanide. By digesting $CdO.M_2O$ in HCyAq: the residue insol. in the acid is said to have the composition $CdCy_2.CdO.5H_2O$ (Joannis, *C. R.* 93, 271).

Double cyanides containing cad-

mium cyanide. The salt $CdCy_2.2KCy$ is produced by adding KCyAq to solution of Cd acetate, evaporating, and crystallising. White octahedra; v. sol. water; unchanged in air at c. 200°. H.F. [Cd, Cy^2, 2KCyAq] = 44,750; [$CdCy^2$Aq, 2KCyAq] = 10,790 (*Th.* 3, 474). Solution gives pps. with various metallic salts, *e.g.* with solution of salts of Ca, Ba, Cu, Mn, Sr, Zn (Rammelsberg, *P.* 38, 364). The double salt $2CdCy_2.Cu_2Cy_2$ is said to be formed by dissolving CdO_2H_2 along with $CuCO_3$ in HCyAq, and evaporating (Schuler, *A.* 87, 48). By dissolving CdO_2H_2 and CuO_2H_2 in HCyAq and allowing the liquid to evaporate in the air, the salt $2CdCy_2.CuCy_2$ is obtained (Schuler, *l.c.*). Various other double salts are described by Schuler (*l.c.*).

Calcium cyanide $Ca(CN)_2$. By heating Ca_2FeCy_6 (Schulz, *J. pr.* 68, 257). A solution of $CaCy_2$ is obtained by adding HCNAq to $CaCO_3$; the solution soon decomposes; if conc., crystals of an oxycyanide separate, $3CaO.CaCy_2,15H_2O$ (Joannis, *C. R.* 92, 1338, 1417). H.F. [CaOAq,2HCyAq] = 6,440; [Ca,Cy^2,Aq] = 115,340 (Joannis, *A. Ch.* [5] 27, 489).

Cerium cyanide, not isolated. KCyAq added to salts of Ce ppts. a white solid which at once decomposes with evolution of HCN, leaving Ce oxide (Beringer, *A.* 42, 139).

Chromium cyanides. Simple cyanides have not been isolated; the pps. obtained by adding KCyAq to $CrCl_2$Aq and $CrCl_3$Aq soon decompose.

Potassium chromocyanide K_4CrCy_6. $CrCO_3$ (obtained by adding K_2CO_3Aq to $CrCl_2$Aq saturated with CO_2, air being excluded) is mixed with KCyAq until the solid has partially dissolved, the yellow liquid is filtered and evaporated (Moissan, *A. Ch.* [6] 4, 136). Long yellow needles; S.G. 1·71; S. (20°) 32 33; insol. alcohol, ether, benzene, and chloroform. Unchanged in air at ordinary temperature. Non-poisonous. Aqueous solution partially decomposed on boiling. Oxidising agents form chromicyanide, K_3CrCy_6; with $FeSO_4$Aq gives red colouration, $\frac{1}{10000}$ part of the salt in a solution may be thus detected (Moissan, *l.c.*). Gives pps. with metallic salts (*v.* also Christensen, *J. pr.* [2] 31, 163).

Potassium chromicyanide K_3CrCy_6. Prepared by oxidising K_4CrCy_6; or by heating KCyAq with Cr alum, or with Cr-K chloride, or by dissolving freshly ppd. $Cr_2O_6H_6$ in acetic acid, evaporating to dryness, dissolving in water, and adding the liquid to hot KCyAq (Kaiser, *A. Supplbd.* 3, 163; Stridsberg, *J.* 1864. 304; Descamps, *A. Ch.* [5] 24, 178; Christensen, *J. pr.* [2] 31, 163). Yellow monoclinic crystals; sol. water, insol. absolute alcohol; easily decomposed by dilute acids. Gives pps. with most metallic salts (*v.* Christensen, *J. pr.* [2] 23, 52).

Ammonium chromicyanide $(NH_4)_3CrCy_6$ (Kaiser, *A. Supplbd.* 3, 163).

Chromocyanhydric acid H_4CrCy_6 (*chromocyanic acid*). Small white crystals, obtained by decomposing the K salt by dilute H_2SO_4Aq; sol. water, solution rapidly decomposes in air (Moissan, *A. Ch.* [6] 4, 136).

According to Descamps (*A. Ch.* [5] 24, 178) salts analogous to *nitroprussides* (*q. v.* p. 340) are produced by passing NO into chromocyanides.

Cobalt cyanides. One simple cyanide, $CoCy_2$, is known; two series of salts derived from cobalto-cyanhydric acid and cobalti-cyanhydric acid have been prepared; the cobaltocyanides are very unstable, while the cobalticyanides are stable salts.

Cobaltous cyanide $Co(CN)_2$. Buff coloured pp. by adding KCy to Co salts, or HCNAq to Co acetate (Wohler, *Gehlen's Journ.* 6, 234). The pp. contains $2H_2O$ which it does not lose till c. 280° (Zwenger, *A.* 62, 157). Dissolves in KCyAq to form K_3CoCy_6, which quickly changes to K_4CoCy_6.

Cobaltocyanhydric acid H_4CoCy_6 (*Cobaltocyanic acid*). Very unstable pp. obtained by decomposing Pb cobaltocyanide by H_2S, filtering, and adding alcohol (Descamps, *Bl.* [2] 31, 49).

Potassium cobaltocyanide K_4CoCy_6. Amethyst-coloured, deliquescent needles; obtained by adding alcohol to a *cold* solution of $CoCy_2$ in a slight excess of conc. KCyAq. Very unstable: easily changes to K_3CoCy_6. Insol. alcohol and ether. Solution gives pps. with many metallic salts; these are probably cobaltocyanides (Descamps, *l.c.*). According to Descamps (*A. Ch.* [5] 24, 178) salts analogous to the *nitroprussides* (*q. v.* p. 340) are obtained by passing NO into cobaltocyanides.

Cobalticyanhydric acid $H_3CoCy_6.xH_2O$ (*Cobalticyanic acid*). Obtained by evaporating the K salt in solution with conc. H_2SO_4, and extracting the residue with alcohol (Zwenger, *A.* 62, 157); or by decomposing the Cu salt by H_2S. Colourless needles; v. e. sol. in water and alcohol; insol. dry ether. Very acid taste. Not decomposed by heating with conc. HClAq or HNO_3Aq, but slowly by hot conc. H_2SO_4, giving sulphates of NH_4 and Co, and evolving SO_2, CO, and CO_2.

Potassium cobalticyanide K_3CoCy_6. Obtained by dissolving $CoCy_2$ or Co_2O_3 in KCyAq, evaporating, and crystallising (Zwenger, *A.* 62, 157). KCy and K_2CO_3 may be removed by decomposing by acetic acid and ppg. by alcohol. Slightly yellow, transparent, rhombic crystals; isomorphous with K_4FeCy_6. E. sol. water, insol. alcohol. S.G. 1·906. Decomposed by strong acids with separation of cobalticyanhydric acid H_3CoCy_6; not decomposed at ordinary temperatures by HClAq or HNO_3Aq. Reduced by Ba-amalgam to K_4CoCy_6.

Cobalticyanides. Besides the K salt the following have been isolated ($X = CoCy_6$):—

$(NH_4)_3X.H_2O$ (Zwenger, *A.* 62, 157).
$[N(CH_3)_4]_3X$ (Claus a. Merck, *B.* 16, 2737).
$Ba_32X.22H_2O$ (Z., *l.c.*); $BaNH_4.X.H_2O$;
$BaK.X.11H_2O$; $BaLi.X.15H_2O$; $Ba_32X.BaO_2H_2$;
$Ba_32X.BaCl_2.16H_2O$ (Weselsky, *B.* 2, 588).
$CaNH_4.X.10H_2O$; $CaK.X.9H_2O$ (W., *l.c.*).
$CrX.5NH_3.1\frac{1}{2}H_2O$ (Christensen, *J. pr.* [2] 23, 52); $CrX.6NH_3$ (Braun, *A.* 125, 153, 197).
$Co_32X.14H_2O$ (Z., *l.c.*); $Co.X.5NH_3\,1\frac{1}{2}H_2O$ (Gibbs a. Genth, *A.* 104, 150, 295; Braun, *l.c.*);
$CoX.6NH_3.\frac{1}{2}H_2O$ (G. a. G., *l.c.*). $Cu_32X.7H_2O$;
$Cu_32X.4NH_3.10H_2O$ (Z., *l.c.*). $Pb_32X.7H_2O$ (Z., *l.c.*); $Pb_32X.6PbO.3H_2O$ (Z., *l.c.*);
$Pb_32X.3PbO_2H_2.11H_2O$; $Pb_32X.Pb(NO_3)_2.12H_2O$;
$PbKX.3H_2O$; $Pb(NH_4)X.3H_2O$ (Schuler, *W. A. B.* 1879 [II]. 302); $Ni_32X.12H_2O$;
$Ni_32X.4H_2O.7H_2O$ (Z., *l.c.*). $Na_3X.2H_2O$ (Z., *l.c.*);

$Na(NH_4).X$ (Weselsky, *B.* 2, 588). $Ag_3.X$; $Ag_3.X\ NH_3.\frac{1}{2}H_2O$ (Z., *l.c.*). $Sr_32X.20H_2O$; $Sr(NH_4).X.10H_2O$; $SrKX.9H_2O$ (W., *l.c.*). Tl_3X (Fron-Müller, *B.* 11, 91). $YX.2H_2O$ (Clœve a. Hœglund, *Bl.* [2] 18, 197).

A fairly general method of preparing cobalticyanides consists in first preparing the *barium salt* $Ba_3(CoCy_6)_2.xH_2O$, decomposing a solution of this by the sulphates of other metals, filtering, and crystallising; the Ba salt is most easily produced by passing HCy gas into a mixture of $CoSO_4$ and $BaCO_3$, filtering, and crystallising (Weselsky, *W. A. B.* 60, 261). Cobalticyanides containing two metals, *e.g.* $(NH_4)Na.CoCy_6$, $BaK.CoCy_6$, are obtained by mixing solutions of the cobalticyanides, evaporating, and crystallising; these salts generally crystallise well (Weselsky, *l.c.*). *Cobaltous cobalticyanide* $Co_3(CoCy_6)_2.14H_2O$ corresponds in composition to ferrous ferricyanide $Fe_3(FeCy_6)_2$ (*q. v.* p. 338) or *Turnbull's blue*; it is a pale red amorphous solid; obtained either by adding K_3CoCy_6Aq to $CoSO_4Aq$ and washing thoroughly with water, or by heating H_3CoCy_6 with conc. H_2SO_4, and adding water before decomposition is complete. This salt loses part of its water at 100°, and turns blue. It is insol. water; decomposed by KOHAq with separation of $CoO.xH_2O$. Dry $Co_3(CoCy_6)_2$ is blue; it combines with water with production of much heat (Zwengler, *A.* 62, 172).

Copper cyanides. Three cyanides of Cu are known, cuprous cyanide, cupric cyanide, and cupro-cupric cyanide; the first-named is the most stable; double compounds of each, especially with NH_3, have been isolated.

Cuprous cyanide Cu_2Cy_2. Formed by adding KCyAq to Cu_2Cl_2 dissolved in HClAq, or to $CuSO_4Aq$ reduced by SO_2; also by the action of HCNAq on freshly ppd. $Cu(OH)_2$ (Rammelsberg, *P.* 42, 131; 85, 145). Prepared, as small lustrous monoclinic crystals, by decomposing $Cu_2Cy_2.PbCy_2$ suspended in water by H_2S, filtering, and allowing the filtrate (which probably contains $H_2Cu_2Cy_4$) to evaporate (Dauber, *A.* 74, 206; Wohler, *A.* 78, 370); the salt $Cu_2Cy_2.PbCy_2$ is obtained by adding a Pb salt to the solution of $Cu_2Cy_2.KCy$, formed by dissolving $Cu(OH)_2$ in KCyAq. Insol. water; sol. HClAq, NH_3Aq, and solutions of NH_4 salts (Pagenstecher, *N. J. T.* [3] 1, 451); ppd. by H_2O from solution in HClAq; decomposed by conc. HNO_3Aq, not by dilute H_2SO_4Aq. Dissolves in alkali cyanides to form double salts, from which it is ppd. by HClAq.

Double cyanides containing cuprous cyanide (sometimes called *cuprosocyanides*):—1. With NH_4CN, forming monoclinic prisms, insol. H_2O—$Cu_2Cy_2.NH_4Cy$ (Lallemand, *C. R.* 60, 1142); $Cu_2Cy_2.2NH_4Cy$ (Dufau, *C. R.* 36, 1099).—2. With KCN—$Cu_2Cy_2.KCN.H_2O$ (Schiff a. Becchi, *A.* 138, 24); $Cu_2Cy_2.2KCN$; $Cu_2Cy_2.6KCN$ (Rammelsberg, *P.* 42, 114; 106, 491); $3Cu_2Cy_2.4KCN$ (Rammelsberg, *P.* 73, 117). The salt $Cu_2Cy_2.KCN.H_2O$ is insol. in H_2O, the others are soluble; the soluble salts give pps. with salts of the heavy metals; *e.g.* with salts of Fe, Pb, Mn. The pps. thus obtained may be regarded as *cuprosocyanides* of iron, &c. Many of the double cyanides containing Cu_2Cy_2 are sometimes called *cuprosocyanides*, and are regarded as salts of the hypothetical cuprosocyanhydric acid $H_2Cu_2Cy_4$: *e.g.* $Cu_2Cy_2.2NH_4Cy$ is often formulated as $(NH_4)_2Cu_2Cy_4$, and is called *ammonium cuprosocyanide*. The chief objection to this view is that the so-called cuprosocyanides are easily decomposed by dilute acids with precipitation of Cu_2Cy_2 and evolution of HCy; hence it seems better to class them with the double cyanides (*e.g.* of Ni) than with the salts of acids the negative radicles of which are composed of metal and cyanogen.—3. With other cyanides—$Cu_2Cy_2.BaCy_2.H_2O$ (Meillet, *J. Ph.* [3] 3, 413; Weselsky, *B.* 2, 588); $Cu_2Cy_2.2CdCy_2$ (Schuler, *A.* 87, 46); compounds with NaCN also exist, but their composition has not been accurately determined (*v.* Meillet, *J. Ph.* [3] 3, 413).

Cupric cyanide $CuCy_2$. This is probably the composition of the yellow pp. obtained by adding KCyAq to solutions of Cu salts; very unstable, decomposing at ordinary temperatures to Cy and $Cu_2Cy_2.CuCy_2$ (Rammelsberg, *P.* 42, 131; 85, 145; Lallemand, *C. R.* 58, 750).

The double cyanide $CuCy_2.2CdCy_2$ is described by Schuler (*A.* 87, 46).

Cupro-cupric cyanide $CuCy_2.Cu_2Cy_2.5H_2O$. Obtained by adding KCyAq to a Cu salt solution and allowing the pp. to remain exposed to the air, or by adding a solution of one of the K cuprous cyanides to a Cu salt (Hadow, *C. J.* 13, 106). Green lustrous crystals, decomposing at 100° to Cu_2Cy_2 with evolution of H_2O and Cy. Acids evolve HCy, ppg. Cu_2Cy_2, and leaving a cupric salt in solution. The fact that this salt may be obtained by adding $2KCy.Cu_2Cy_2(K_2Cu_2Cy_4)$ to solution of a Cu salt suggests that $CuCy_2.Cu_2Cy_2$ may be the cupric salt of the hypothetical cuprosocyanhydric acid $H_2Cu_2Cy_4$; if this view is adopted the salt in question would be formulated as $Cu.Cu_2Cy_4$ and called *cupric cuprosocyanide*.

The compounds $CuCy_2.Cu_2Cy_2.H_2O$ and $CuCy_2.2Cu_2Cy_2.H_2O$ have been described (Dufau, *C. R.* 36, 1099; Lallemand, *C. R.* 58, 750).

Double compounds of cupro-cupric cyanide with ammonia. The following have been isolated ($X = CuCy_2.Cu_2Cy_2$):—$X.2NH_3.H_2O$; $X.4NH_3$; $X.6NH_3$ (Dufau, *C. R.* 36, 1099). $X.3NH_3$ (Mills, *Z.* 1862. 515). Also $CuCy_2.2Cu_2Cy_2.4NH_3.2H_2O$ (Hilkenkamp, *A.* 97, 218). These ammoniacal compounds are sometimes looked on as salts of the hypothetical cuprosocyanhydric acid $H_2Cu_2Cy_4$; they are supposed to be obtained by replacing H by complex radicles containing Cu derived from xNH_4. On this view the compounds in question may be formulated and named as follows:—

$(N_2H_6Cu).Cu_2Cy_4$, *cuprodiammonio-cuprosocyanide* ($= CuCy_2.Cu_2Cy_2.2NH_3$).

$(N_2H_4(NH_4)_2Cu).Cu_2Cy_4$, *cuprotetrammonio-cuprosocyanide* ($= CuCy_2.Cu_2Cy_2.4NH_3$).

$(N_2H_2(NH_4)_4Cu).Cu_2Cy_4$, *cuprohexammonio-cuprosocyanide* ($= CuCy_2.Cu_2Cy_2.6NH_3$).

Gold cyanides. Aurous cyanide AuCy, and several double cyanides of AuCy are known; also auricyanhydric acid $HAuCy_4$ and its salts.

Aurous cyanide AuCy. Prepared by evaporating AuCy.KCy with HClAq, and washing the residue with water; AuCy.KCy is obtained by dissolving finely divided Au or Au_2O in KCyAq. AuCy is also obtained by heating $Au_2O.xH_2O$ with HCNAq (Himly, *A.* 42, 157, 337). Citron-yellow crystalline powder; insol. water, alcohol, or ether. Heated it gives Au and Cy. Not acted on by hot HClAq, HNO_3Aq, or H_2SO_4Aq; slowly decomposed by *aqua regia*; not acted on by H_2S; sol. $(NH_4)_2S_2Aq$, from which solution acids ppt. Au_2S. Decomposed by hot KOHAq to Au and a solution of AuCy.KCy. Sol. hot NH_3Aq, and in alkali thiosulphates.

Double cyanides containing aurous cyanide: AuCy.KCy; obtained by dissolving AuCy, Au_2O, or finely divided Au, in KCyAq, and evaporating (Himly, *A.* 42, 157, 337; Bagration, *J. pr.* 31, 367; Elsner, *J. pr.* 37, 333). Colourless, transparent, rhombic octahedra. E. sol. water, sl. sol. alcohol, insol. ether (Glassford a. Napier, *P. M.* [3] 25, 71). Decomposed by warming with acids, giving pp. of AuCy. Iodine dissolves in AuCy.KCyAq, when excess of I is added and the liquid cooled dark brownish violet crystals separate of $AuCy.KCy.I_2$; analogous compounds are obtained by adding excess of Br or Cl to AuCy.KCyAq. These compounds may be regarded as K salts of the hypothetical iodo-, bromo-, and chloro-auricyanhydric acids $HAuCy_2X_2$ (X = I, Br, or Cl) (*v.* Lindbom, *B.* 10, 1725; Blomstrand, *J. pr.* [2] 3, 213). The following double cyanides are also known; most of them combine with I_2, Br_2, and Cl_2; $AuCy.NH_4Cy$ (Himly, *A.* 42, 157, 337; Lindbom, *B.* 10, 1725); $2AuCy.BaCy_2.2H_2O$; $2AuCy.CaCy_2.3H_2O$; $2AuCy.CdCy_2$; $2AuCy.CoCy_2$; AuCy.NaCy; $2AuCy.SrCy_2.3H_2O$; $2AuCy.ZnCy_2$ (Lindbom, *B.* 10, 1725). A number of other double cyanides of Au are described by Lindbom (*Bl.* [2] 29, 416).

Auricyanhydric acid $HAuCy_4.3H_2O$. Large white tablets; obtained by ppg. $KAuCy_4$ by $AgNO_3Aq$, and decomposing the pp. by less than an equivalent quantity of cold HClAq. Sol. water, alcohol, and ether. Melts at 50°, decomposing at a higher temperature to AuCy and HCy, and then to Au and Cy. Solution gives AuCy on heating (*v.* Lindbom, *B.* 10, 1725).

Auricyanides (Himly, *A.* 42, 157, 337; Lindbom, *l.c.*). $NH_4.AuCy_4.H_2O$. $KAuCy_4.1\frac{1}{2}H_2O$; formed by adding perfectly neutral $AuCl_3Aq$ to warm conc. KCyAq; colourless tablets, v. sol. hot water, insol. absolute alcohol: loses all H_2O at 200°, and at the same time decomposes to AuCy.KCy and Cy. $AgAuCy_4$; yellow pp. formed by adding $AgNO_3Aq$ to $KAuCy_4Aq$; insol. HNO_3Aq, sol. NH_3Aq. $Co(AuCy_4)_2$.

Indium cyanide. Pp. obtained by adding KCyAq to an In salt solution; sol. excess of KCyAq; on evaporating this liquid all In is ppd. as hydroxide (Meyer, *J.* 1868. 244).

Iridium cyanides. The cyanide $IrCy_3$ is known, also iridium cyanhydric acid H_3IrCy_6 and its salts (*v.* Martius, *A.* 117, 357; Claus, *J.* 1855. 444; Wohler a. Booth, *P.* 31, 161; Rammelsberg, *P.* 42, 140).

Iridium cyanide $IrCy_3$. Green powder, obtained by decomposing H_3IrCy_6Aq by HClAq.

Iridium cyanhydric acid H_3IrCy_6. Obtained by decomposing the Ba salt (*q. v.*) by H_2SO_4Aq, filtering and adding ether. Crystallises from ether in white crystalline crust; e. sol. alcohol and water. Decomposes at 300°, evolving HCN. Decomposed by HClAq giving pp. of $IrCy_3$.

Iridicyanides K_3IrCy_6; obtained by fusing $IrCl_4.2NH_4Cl$ with $1\frac{1}{2}$ pts. KCy for 10-15 min., treating fused mass with water, filtering, and crystallising. Very stable salt; crystallises in orthorhombic prisms; insol. alcohol (W. a. B.).

$Ba_3(IrCy_6)_2.18H_2O$; obtained by fusing $IrCl_4.2NH_4Cl$ with $1\frac{1}{2}$ pts. KCy; allowing to cool, dissolving in water, adding HClAq, ppg. by addition of $CuSO_4Aq$, washing pp. and digesting it with excess of BaO_2H_2, passing CO_2 through the liquid, filtering and crystallising; the first crop of crystals generally contains Ba platinocyanide, the second crop is free from this salt. Crystallises in prisms, which effloresce in air, losing $12H_2O$; very stable salt.

A solution of H_3IrCy_6 gives pps. with salts of many heavy metals.

Iron cyanides. No simple cyanide of Fe has been isolated with certainty. Addition of KCyAq to solution of a ferrous salt produces a yellow-red to brown-red pp., which is probably $FeCy_2$, but always contains K (Fresenius, *A.* 106, 210); when the ferrous salt is in slight excess the composition of the pp. approximates to $KFeCy_3$ (Stadeler, *A.* 151, 1). KCyAq added to solution of a ferric salt ppts. $Fe_2O_6H_6$ (Haidlen a. Fresenius, *A.* 42, 130). If iron cyanides exist they are very unstable. Very many compound cyanides of iron with other metals have been prepared; these belong to the class of stable compound cyanides which are not resolved by acids into their constituent cyanides; as a rule their reactions are similar to those of ordinary salts, *e.g. cf.* the reaction of K_4FeCy_6Aq with $CuSO_4Aq$, giving $CuFeCy_6$ and K_2SO_4Aq, with that of $BaCl_2Aq$ and Na_2SO_4Aq, giving $BaSO_4$ and NaClAq. The compound cyanides of iron are generally more stable than their constituent cyanides. This is shown, among other ways, by looking at the thermal changes which accompany the production of these double cyanides. Thus, the heat of formation of solid K_4FeCy_6 from 4K + Fe + 6Cy is c. 367,000 (Berthelot, *C. R.* 91, 82), the heat of formation of 4KCy (solid) from 4K + 4Cy is c. 270,000. We have then

$$[K^4, Fe, Cy^6] = 367,000$$

$$[K^4, Cy^4] = 270,000$$

$$\text{hence} \quad [4KCy, Fe, Cy^2] = 97,000$$

Now the heat of formation of a ferrous salt is generally somewhat less than that of the corresponding Zn salt; but $[Zn, Cy^2]$ = c. 53,000 (solid $ZnCy_2$), therefore we may provisionally conclude that $[Fe, Cy^2]$ = c. 50,000.

Now if $[4KCy, Fe, Cy^2] = 97,000$ and $[Fe, Cy^2] = 50,000$, it follows that $[4KCy, FeCy^2] = 17,000$: that is the combination of 4KCy with $FeCy_2$ to produce K_4FeCy_6 is accompanied by the production of a quantity of heat roughly equal to 47,000 gram-units. This quantity of heat is much larger than that generally produced in the formation of double salts; *e.g.* $[KCy, AgCy] = 11,200$, $[HgCyAq, 2KCyAq] = 12,000$, $[HgI^2, 2KI] = 3,000$, $[ZnSO^4, K^2SO^4] = 4,000$. Hence on the thermal evidence alone we might provisionally conclude that K_4FeCy_6 does not belong to the class of double salts.

In considering the compound cyanides of iron, it is advantageous to begin with the two typical salts, potassium ferrocyanide K_4FeCy_6 and potassium ferricyanide K_3FeCy_6. K_3FeCy_6 is produced by the action of oxidisers on K_4FeCy_6, and reducing agents change K_3FeCy_6 to K_4FeCy_6. To each of these salts there corresponds an acid,

H_4FeCy_6 and H_3FeCy_6 respectively. These acids have been isolated, and from each has been obtained a great many salts and double salts. Some of these salts form derivatives, *e.g.* the *nitroprussides*; and finally there are a few compound iron cyanides not belonging to either of the two main classes.

We shall consider first *ferrocyanhydric acid* H_4FeCy_6, and its salts, the *ferrocyanides*; then *ferricyanhydric acid*, H_3FeCy_6, and its salts, the *ferricyanides*; then the *nitroprussides*; and finally the *perferrocyanides*.

The ferro- and ferri- cyanides are described in alphabetical order; double salts are also described in alphabetical order, thus barium potassium ferrocyanide is described under barium ferrocyanides, but strontium-potassium ferrocyanide under potassium ferrocyanides.

FERROCYANHYDRIC ACID AND FERROCYANIDES.

Ferrocyanhydric acid H_4FeCy_6. (*Ferrocyanic acid. Hydroferrocyanic acid. Ferroprussic acid. Hydrogen ferrocyanide.*) Discovered by Porret in 1814 (*T.* 1814. 527).

Formation.—1. Ba_2FeCy_6 is decomposed by an equivalent of H_2SO_4Aq (Porret, *l.c.*).—2. Cu_2FeCy_6 or Pb_2FeCy_6 is decomposed by H_2S (Berzelius, *S.* 30, 44).—3. Prussian blue is decomposed by conc. HClAq, the solution is separated from Fe_2O_3, and evaporated (Robiquet).

Preparation.—To a cold conc. aqueous solution of K_4FeCy_6, which has been boiled to expel air, is added a slight excess of cold conc. air-free HClAq; ether is then added, whereby from 96 to 100 p.c. of the H_4FeCy_6 produced is ppd.; the pp. is washed with HClAq and then with ether; it may be recrystallised by dissolving in alcohol and adding ether; all operations should be conducted as far as possible in absence of O (Posselt, *A.* 42, 163; *v.* also Liebig, *A.* 87, 127; Dolfus, *A.* 65, 221).

Properties and Reactions.—White crystalline powder; becomes blue in moist air, with evolution of HCN and production of Prussian blue, Fe_7Cy_{18} (Reimann a. Carius, *A.* 113, 39). Unchanged in sunlight in an atmosphere of H. Soluble in water; solution is strongly acid to litmus; it decomposes carbonates, acetates, tartrates, and oxalates. H_4FeCy_6 is a strong acid; relative affinity not very much less than that of HCl (*v.* Ostwald's *Lehrbuch*, 2, 851). When boiled with water is decomposed to HCN and white $FeH_2(FeCy_6)$ (R. a. C., *l.c.*). Berthelot (*C. R.* 91, 82) gives H.F. of the acid in solution as $[H^4,Fe,4CN,Aq] = 107{,}200$; and the heat of neutralisation (*C. R.* 78, 1085) as $[H^4FeCy^6Aq, 4KOHAq] = 54{,}000$. Ferrocyanhydric acid is tetrabasic, forming salts $M^I_4FeCy_6$, $M^{II}_2FeCy_6$, $M^{II}M^I_2.FeCy_6$, &c.

Ferrocyanides (*Ferroprussiates*). *Salts of ferrocyanhydric acid* H_4FeCy_6. These salts are not to be regarded as double cyanides; *v.* remarks *supra.* Many ferrocyanides are coloured; the production of one of these salts by adding K_4FeCy_6 to a metallic salt solution is often used as a test for different metals. The soluble alkali ferrocyanides are not poisonous. Those ferrocyanides which are completely dehydrated by heat without decomposition are decomposed at higher temperatures into N and Fe carbide, and either a cyanide of the other metal, *e.g.* K_4FeCy_6, or N and metallic carbide, *e.g.* $PbFeCy_6$, or Cy and metal, *e.g.* Ag_4FeCy_6. Those ferrocyanides which cannot be completely dehydrated without decomposition are resolved at a high temperature into HCN, CO_2, NH_3, and either a mixture or compound of each of the metals with C. When aqueous solutions of the alkali ferrocyanides are electrolysed alkali separates at the negative pole, and HCN and Prussian blue at the positive pole; if the positive pole is Cu, $CuCy_2$ is formed. Heated with conc. H_2SO_4 ferrocyanides give SO_2, CO, CO_2, and N, and form sulphates of NH_4, Fe, and the other metal of the original salt. Some ferrocyanides are decomposed by H_2S giving metallic sulphides and ferrocyanhydric acid, *e.g.* Pb_2FeCy_6. Ferrocyanides of heavy metals are generally decomposed by aqueous alkali, giving alkali ferrocyanides and a pp. of the hydrated oxide of the heavy metal.

Aluminium ferrocyanide $Al_4(FeCy_6)_3.xH_2O$ (Wyrubow, *A. Ch.* [5] 8, 444; Tissier, *C. R.* 45, 232). By mixing conc. solutions of alum and K_4FeCy_6; many reactions have been tried to give an Al salt, but there is doubt as to the isolation of a definite salt.

Ammonium ferrocyanide $(NH_4)_4FeCy_6.6H_2O$. Produced by action of NH_3Aq on Prussian blue (Scheele), or by adding $(NH_4)_2CO_3$ to Pb_2FeCy_6 (Berzelius). Best prepared by neutralising H_4FeCy_6Aq by NH_3Aq, and adding alcohol (Bette, *A.* 23, 120; *v.* also Bunsen, *P.* 36, 404). White crystals, isomorphous with K_4FeCy_6; sol. in water, insol. in alcohol.

Double salts $(NH_4)_4FeCy_6.2NH_4Cl.3H_2O$, and $(NH_4)_4FeCy_6.2NH_4Br.3H_2O$; obtained by mixing solutions of the constituent salts and cooling (Bunsen, *P.* 36, 404; Himly a. Bunsen, *P.* 38, 208: crystalline forms are given).

Double ferrocyanides of ammonium $(NH_4)_2CuFeCy_6$ (Schulz, *J. pr.* 68, 257). $(NH_4)_2Li_2.FeCy_6.3H_2O$ (Wyrubow, *A. Ch.* [4] 21, 271). $(NH_4)K_3.FeCy_6.3H_2O$; obtained by acting on K_4FeCy_6Aq in presence of NH_3 by lactose or glucose until the solution is yellow, and then adding alcohol (Reindel, *J. pr.* 65, 450) $(NH_4)_2K_2.FeCy_6.3H_2O$; by decomposing $BaK_2.FeCy_6$ (*v. Barium ferrocyanide*) by $(NH_4)_2SO_4Aq$, or by treating $FeK_2.FeCy_6$ with NH_3Aq (Reindel, *J. pr.* 76, 342; 100, 6; Playfair, *J. pr.* 69, 287).

Antimony ferrocyanide $Sb_4(FeCy_6)_3.25H_2O$ (Atterberg, *Bl.* [2] 24, 355). Yellow pp. by adding $SbCl_3$ to K_4FeCy_6Aq.

Barium ferrocyanide $Ba_2FeCy_6.6H_2O$ (Berzelius, *Lehrb.* 4, 400 [4th ed.]; Wyrubow, *A. Ch.* [4] 16, 280). Formed by passing air over a heated mixture of C and $BaCO_3$, and then acting with $FeSO_4$; by boiling Prussian blue with BaOAq, filtering, and crystallising by cooling; or by boiling K_4FeCy_6Aq with an equivalent quantity of $BaCl_2$, filtering, and cooling. Yellow monoclinic prisms; sol. in 1,000 parts water at 15°, and in 100 parts at 75°.

Double ferrocyanides of barium $BaK_2.FeCy_6.3H_2O$ (Bunsen, *P.* 36, 404; Reindel, *J. pr.* 76, 342; Mosander, *P.* 25, 390; Duflos, *S.* 65, 233). Crystallises with $5H_2O$ according to Wyrubow (*A. Ch.* [4] 21, 271). By mixing conc. solutions of $BaCl_2$ and K_4FeCy_6, the latter in excess. Reacts with soluble sulphates giving $BaSO_4$ and double ferrocyanides of the form $M^{II}K_2.FeCy_6$ (Reindel, *l.c.*).

Beryllium ferrocyanide $Be_2FeCy_6.4BeO_2H_2.7H_2O$ (Atterberg, *Bl.* [2] 19, 497; *cf.* Toczynsky, *Z.* 1871. 276). By the action of $BeSO_4Aq$ on Pb_2FeCy_6 in presence of NH_3.

Bismuth ferrocyanides. $Bi_4(FeCy_6)_3$; almost colourless salt obtained by adding solution of $Bi3NO_3$ in smallest excess of air-free HNO_3Aq to air free K_4FeCy_6Aq, in cooled flask, washing with air-free water in atmosphere of CO_2 and drying over H_2SO_4 *in vacuo* (Pattison Muir, *C. J.* [2] 16, 651; 17, 40). Salt soon decomposes when moist, giving off HCN and forming Prussian blue. Decomposed by Cl or Br in presence of alkali. Changed by Cl or dilute HNO_3Aq in the cold to ferricyanide $Bi_4(FeCy_6)_5$. Wyrubow (*A. Ch.* [5] 8, 444) says that $Bi_2FeCy_6.5H_2O$ is produced by action of $Bi3NO_3$ with H_4FeCy_6; but the data are meagre.

Double ferrocyanide of bismuth. According to Wyrubow (*l.c.*) addition of K_4FeCy_6 to $Bi(NO_3)_3$ in HNO_3Aq ppts. $BiK.FeCy_6.4H_2O$; the existence of this salt wants confirmation.

Cadmium ferrocyanides. None isolated.

Double ferrocyanides of cadmium $CdK_2FeCy_6.H_2O$ (Hermann, *A.* 145, 235); or $Cd_3K_5(FeCy_6)_4.11H_2O$ (?) (Wyrubow, *A. Ch.* [5] 8, 444). By adding K_4FeCy_6Aq to solution of a Cd salt.

Calcium ferrocyanide $Ca_2(FeCy_6).12H_2O$. Triclinic crystals; sol. in 2 parts of water at 90°; by decomposing Prussian blue by CaOAq, filtering, exposing to the air, filtering from $CaCO_3$, and evaporating (Wyrubow, *A. Ch.* [4] 16, 280; Berzelius, *S.* 30, 12).

Double ferrocyanides of calcium $CaK_2.FeCy_6.3H_2O$ (Mosander, *P.* 25, 390; Marchand, *J. Chim. Méd.* 20, 558); by ppg. a Ca salt by excess of K_4FeCy_6Aq. $CaNa_6(FeCy_6)_2$ (Wyrubow, *A. Ch.* [4] 21, 271). $CaSrFeCy_6.10H_2O$ (W., *l.c.*).

Cerium ferrocyanide $Ce_4(FeCy_6)_3.30H_2O$ (Wyrubow, *A. Ch.* [5] 8, 444). Double ferrocyanides of Ce and K are also said to exist; but none of the salts has been thoroughly examined (*v.* Jolin, *Bl.* [2] 21, 535).

Chromium ferrocyanides. Addition of K_4FeCy_6Aq to $CrCl_2Aq$ gives a yellow pp. probably Cr_2FeCy_6 (Stridsberg, *J.* 1864. 304; *cf.* Kaiser, *A. Supplbd.* 3, 163).

Cobalt ferrocyanides. K_4FeCy_6Aq added to a Co salt solution produces a blue pp. which soon changes in air to reddish; this pp. is a ferrocyanide of Co, but the exact composition has not been accurately determined. Wyrubow (*A. Ch.* [5] 8, 444) gives the formulæ $Co_2FeCy_6.7H_2O$, $Co_7(FeCy_6)_4.22H_2O$, $CoK_2.FeCy_6$, and $Co_5K_6(FeCy_6)_4$, to the pp. obtained under different conditions. Compounds of Co ferrocyanides with NH_3 are described by Curda (*Z.* 1869. 369), and by Gintl (*Z.* 1868. 525); the formulæ $Co_2FeCy_6.12NH_3.9H_2O$, and $Co_2FeCy_6.8NH_3.10H_2O$ are given; a salt having the composition $Co_2FeCy_6(NO_2)_2.10NH_3.7H_2O$ is described by Gibbs a. Genth (*A.* 104, 150, 295; *cf.* Braun, *A.* 132, 33).

Copper ferrocyanides. The brown-red pp. obtained by adding K_4FeCy_6 to a Cu salt solution is more or less pure Cu_2FeCy_6; it is better prepared by using H_4FeCy_6Aq, as the pp. obtained by K_4FeCy_6 is mixed with Cu-K ferrocyanides (*v.* Williamson, *A.* 57, 225). The pp. dried over H_2SO_4 is said to contain $7H_2O$ (Rammelsberg, *P.* 74, 65), or $9H_2O$ (Mouthiers, *A.* 64, 297), or $10H_2O$ (Wyrubow, *A. Ch.* [5] 8, 444). If an excess of K_4FeCy_6 is used as pptant., double Cu-K ferrocyanides are obtained; the formulæ $CuK_2.FeCy_6.H_2O$, and $Cu_3K_2(FeCy_6)_2.12H_2O$, are given (Rammelsberg, *P.* 74, 65; Schulz, *J. pr.* 68, 257; Wyrubow, *A. Ch.* [5] 8, 444; Reindel, *J. pr.* 103, 166). The salt $CuNa_2FeCy_6$ is described by Schulz (*l.c.*).

Double compounds of cupric ferrocyanide. By ppg. an ammoniacal solution of CuO by K_4FeCy_6, the salt $Cu_2FeCy_6.4NH_3.H_2O$ is formed (Bunsen, *P.* 34, 134; Mouthiers, *A.* 64, 297). By digesting Cu_2FeCy_6 with NH_3Aq crystalline $Cu_2FeCy_6.8NH_3.H_2O$ is formed (Mouthiers, *l.c.*; Guyard, *Bl.* [2] 31, 438).

Cuprous ferrocyanide. This salt is said to be formed by adding K_4FeCy_6Aq to Cu_2Cl_2 in HClAq; it probably has the composition Cu_4FeCy_6 (Proust). The following double cuprous-potassium (and sodium) ferrocyanides have been obtained:— $Cu_2K_2.FeCy_6.1\frac{1}{2}H_2O$; $Cu_2Na_2.FeCy_6$ (Schulz, *J. pr* 68, 257); $CuK_3.FeCy_6.xH_2O$ (Bolley, *A.* 106, 228; Wonfor, *C. J.* 15, 357).

Didymium and *Erbium ferrocyanides.* The double ferrocyanides $DiK.FeCy_6.4H_2O$, and $ErK.FeCy_6.4H_2O$ are said to be produced by adding K_4FeCy_6Aq to salts of Di and Er respectively (Clève, *Bl.* [2] 21, 196; Clève a. Hoeglund, *Bl.* [2] 18, 197).

Iron ferrocyanides. Ferrous ferrocyanide, $Fe_2.FeCy_6$; and ferric ferrocyanide, $Fe_4(FeCy_6)_3$, are both known; also derivatives of both. In connexion with these compounds *cf.* IRON FERRICYANIDES, p. 338.

Ferrous ferrocyanide $Fe_2.FeCy_6$. Obtained by ppg. ferrous salts by H_4FeCy_6; if K_4FeCy_6 is used the pp. always contains K. Also formed when Prussian blue reacts with H_2S. It is obtained pure by boiling H_4FeCy_6Aq in absence of air (Aschoff, *Ar. Ph.* [2] 106, 257). [$3H_4FeCy_6 = Fe_2.FeCy_6 + 12HCN$.] White amorphous pp. soon oxidised in air with production of blue-coloured compounds; reaction may perhaps be $3(Fe_2.FeCy_6) + 3O + 3H_2O = Fe_2(OH)_6 + Fe_4(FeCy_6)_3$ (Erlenmeyer, *Lehrbuch der organ. Chemie* [1867], 148 *et seq.*).

Double ferrocyanide derived from ferrous ferrocyanide.

Potassium-ferrous ferrocyanide $K_2Fe.FeCy_6$. (*Everitt's salt.*) Obtained by decomposing K_4FeCy_6 with hot dilute H_2SO_4Aq, in making HCN [$2K_4FeCy_6Aq + 3H_2SO_4Aq = 6HCN + 3K_2SO_4Aq + K_2Fe.FeCy_6$] (Williamson, *A.* 57, 225; Everitt, *P.M.* [3] 6, 97). White microscopic quadratic crystals, becoming blue in air; oxidisers produce potassium-ferrous ferricyanide, $FeK.FeCy_6$. Also produced by boiling H_4FeCy_6Aq with K_2SO_4 (Aschoff, *Ar. Ph.* [2] 106, 257); probably always present in the white-blue pp. obtained by adding K_4FeCy_6Aq to ferrous salts (Aschoff, *l.c.*).

Ferric ferrocyanide $Fe_4(FeCy_6)_3$. (*Prussian blue.*) This body was accidentally discovered in 1704 by Diesbach, a colour-maker in Berlin. It was afterwards found that the blue compound could be prepared by calcining blood with potash and then adding sulphate of iron.

In 1724 Woodward of London prepared the colouring matter by deflagrating cream of tartar with nitre, calcining the residue with ox-blood, dissolving in water, and ppg. by alum and sulphate of iron; he thus obtained a greenish pp. which turned blue when treated with hydrochloric acid. More or less pure ferric ferrocyanide is obtained commercially by mixing K_4FeCy_6Aq with partially oxidised ferrous sulphate, and oxidising the light-blue pp. thus formed by exposure to air or by the action of Cl, HNO_3Aq, *aqua regia*, or alkaline hypochlorites; the blue body thus formed, known commercially as *Prussian blue*, is a mixture of ferric ferrocyanide, $Fe_4(FeCy_6)_3$, with ferrous ferro-cyanide $Fe_2.FeCy_6$, ferrous ferricyanide $Fe_3(FeCy_6)_2$ (known commercially as *Turnbull's blue*), and probably one or more of the K-Fe ferro- or ferri-cyanides (*v. post*). The simultaneous production of iron ferrocyanide (Prussian blue) and iron ferricyanide (Turnbull's blue) is probably explained by the fact that both ferrous and ferric salts are present, and that ferric salts oxidise ferro- to ferri-cyanides, while ferrous salts reduce ferri- to ferro- cyanides (*v.* Skraup, *W. A. B.*, 74 (2nd part) *Juniheft*, 1876). The blue pp. obtained by adding K_4FeCy_6Aq to excess of a ferric salt solution is nearly pure ferric ferrocyanide, $Fe_4(FeCy_6)_3$; as thus prepared the substance is known commercially as *Paris blue*. The name *Prussian blue* is often extended to all the blue pps. obtained by adding iron salts to K ferro- or ferri-cyanide. For an account of the manufacture of Prussian blues *v.* DICTIONARY OF TECHNICAL CHEMISTRY.

Formation.—1. By the reaction of ferric salts with K_4FeCy_6Aq (*v. supra*); if the ferric salt is kept in excess, approximately pure $Fe_4(FeCy_6)_3$ is obtained; if the K_4FeCy_6 is in excess the pp. always contains K-Fe ferrocyanide, $K_2Fe.FeCy_6$.—2. By adding a ferrous and a ferric salt to KCyAq, or to HCyAq with excess of KOH added, and then adding acid to dissolve the $Fe(OH)_2$ and $Fe(OH)_3$ ppd. by the KOH or the KCy. [$18KCyAq + 3FeSO_4Aq = 3K_4FeCy_6Aq + 3K_2SO_4Aq$; $3K_4FeCy_6Aq + 4FeCl_3Aq = 12KClAq + Fe_4(FeCy_6)_3$.]—3. The action of air, or other oxidiser, on H_4FeCy_6, or on ferrous ferrocyanide, $Fe_2.FeCy_6$, forms $Fe_4(FeCy_6)_3$.

Preparation. — K_4FeCy_6Aq is added to $FeCl_3Aq$ keeping the latter in excess; the pp. is digested with $FeCl_3Aq$, to remove any $K_2Fe.FeCy_6$, thoroughly washed and dried. Or H_4FeCy_6 is used in place of K_4FeCy_6; in this case the pp. is pure $Fe_4(FeCy_6)_3$.

Properties. — Dark-blue amorphous solid with lustre resembling that of copper. Obtained in lustrous crystals by spontaneous evaporation of solution in conc. HClAq (Gintl, *D. P. J.* 235, 248). Does not become perfectly dehydrated until heated to c. 250°; complete dehydration is accompanied by partial decomposition, with evolution of NH_4Cy and $(NH_4)_2CO_3$ (*v.* Reimann a. Carius, *A.* 113, 39; Skraup, *A.* 186, 371; Rammelsberg, *A.* 64, 298). Strongly heated it glows and is burnt to Fe_2O_3. Insoluble in water, alcohol, ether, oils, and dilute acids; sol. in conc. HClAq, addition of water ppts. the original compound; sol. in $H_2C_2O_4Aq$, also in (NH_4) tartrate solution; is entirely ppd. from solution in $H_2C_2O_4Aq$ by exposure to sunlight (Schoras, *B.* 3, 12).

Reactions.—1. *Heat* alone decomposes $Fe_4(FeCy_6)_3$, evolving CO_2, CO, NH_4Cy, HCN, and $(NH_4)_2CO_3$.—2. *Heated in air* it is burnt to Fe_2O_3, NH_4Cy, and CO_2.—3. Decomposed by *alkalis* (including MgO) to Fe_2O_3 and K_4FeCy_6Aq; similar change is effected by K_2CO_3Aq, and by excess of NH_3Aq.—4. Boiled with *mercuric oxide and water*, Fe_2O_3 and $HgCy_2$ are formed.—5. With *lead oxide*, Fe_2O_3, Pb_2FeCy_6, and K_3FeCy_6 are produced.—6. Reduced *by sulphuretted hydrogen*, also by *iron* or *zinc*, to white ferrous ferrocyanide $Fe_2.FeCy_6$. For account of *Soluble Prussian blue v. Potassium-ferrous ferricyanide* under *Ferrous ferricyanide.*

Double ferrocyanide derived from ferric ferrocyanide.

Ammonio-ferric ferrocyanide $Fe_4.(FeCy_6)_3.6NH_3.9H_2O$ (Mouthiers, *J. Ph.* 9, 262). When excess of NH_3Aq is added to $FeCl_2Aq$ and the liquid is filtered into K_4FeCy_6Aq, a white pp. forms which soon becomes blue in the air; this blue solid when heated with NH_4 tartrate solution at 60°–80° for some hours to dissolve $Fe_2O_6H_6$ leaves blue ammonio-ferric ferrocyanide, which is washed with water, and dried below 100°. The compound evolves HCN at 100°; no NH_3 is evolved below 160°. The same compound is the first product of the action of NH_3Aq on $Fe_4(FeCy_6)_3$ (Mouthiers, *l.c.*). Because of the stability of this compound it may perhaps be regarded as *ferric-ferric-ammonium ferrocyanide* $(Fe_2.N_6H_{18}Fe_2)(FeCy_6)_3$.

Lanthanum ferrocyanide.—None has been isolated, but the double salt $LaK.FeCy_6.4H_2O$ is described by Clève (*Bl.* [2] 21, 196; *v.* also Wyrubow, *A. Ch.* [5] 8, 444).

Lead ferrocyanide $Pb_2FeCy_6.3H_2O$. White pp. formed by adding K_4FeCy_6Aq to $Pb(NO_3)_2Aq$ and washing repeatedly with water (Berzelius; Wyrubow, *A. Ch.* [5] 8, 444). Loses all H_2O at moderate temperature. Dehydrated salt heated in air evolves N and leaves mixture of carbides of Fe and Pb.

Lithium ferrocyanide $Li_4.FeCy_6.9H_2O$; very soluble salt; deliquescent crystals (Wyrubow, *A. Ch.* [4] 16, 280). The *double salt* $Li_2K_2.FeCy_6.3H_2O$ is described by Wyrubow (*A. Ch.* [4] 21, 271).

Magnesium ferrocyanide $Mg_2.FeCy_6.12H_2O$. By dissolving $MgCO_3$ in H_4FeCy_6Aq and evaporating; pale yellow crystals; sol. 3 pts. cold water; unchanged in air (Bette, *A.* 22, 148; 23, 115). The *double salt* $MgK_2.FeCy_6$ is described by Berzelius (*Lehrb.* 4, 400 [4th ed.]).

Manganese ferrocyanide $Mn_2FeCy_6.7H_2O$; white pp. by adding K_4FeCy_6Aq to solution of a manganous salt (Wyrubow, *A. Ch.* [5] 8, 444; Mosander, *P.* 25, 390).

Manganese-potassium ferrocyanide $MnK_2.FeCy_6$ (Berzelius; Wyrubow, *l.c.*).

Mercury ferrocyanides. Mercurous and mercuric salts give pps. with K_4FeCy_6, but the composition of the pps. was not accurately determined. Bunsen (*P.* 34, 134) obtained a *compound of ammonia with mercuric ferrocyanide* $Hg_2FeCy_6.2NH_3.H_2O$ by mixing cooled solutions of $Hg(NO_3)_2Aq$, NH_3Aq, and NH_4NO_3Aq.

Molybdenum ferrocyanides $Mo_2FeCy_6.8H_2O$; $Mo_2FeCy_6.14H_2O$; $Mo_4FeCy_6.20H_2O$; and the *double salt* $Mo_4K_2FeCy_6.20H_2O$ (?) (Wyrubow, *A. Ch.* [5] 8, 444; *cf.* Atterberg, *Bl.* [2] 24, 355). These salts are said to be formed by reactions between K_4FeCy_6Aq and salts of Mo, or in some cases NH_4 molybdate; their composition is doubtful.

Nickel ferrocyanides. According to Wyrubow (*A. Ch.* [5] 8, 444) K_4FeCy_6, added to a salt of Ni, ppts. $NiK_2.FeCy_6.3H_2O$; if excess of ferrocyanide is used the salt is said to have the composition $Ni_4K_2FeCy_6.6\frac{1}{2}H_2O$. By using H_4FeCy_6Aq in place of the K salt, salts are obtained which Wyrubow formulates as $Ni_7(FeCy_6)_4$ and $Ni_2FeCy_6.11(\text{or } 14)H_2O$. By adding K_4FeCy_6Aq to a Ni salt solution containing NH_3 various salts are formed, and from these again others are obtained by treatment with NH_3Aq; the following are described:— $Ni_2FeCy_6.10NH_3.4H_2O$; $Ni_2FeCy_6.4NH_3.H_2O$ (Reynoso, *A. Ch.* [3] 30, 252); $Ni_2FeCy_6.2NH_3.4(\&9)H_2O$; $Ni_2FeCy_6.8NH_3.4H_2O$; $Ni_2FeCy_6.12NH_3.9H_2O$ (Gintl, *Z.* 1868. 525).

Niobium ferrocyanides.—None certainly isolated. Several *double salts* are described (Wyrubow, *A. Ch.* [5] 8, 444; Atterberg, *Bl.* [2] 21, 356); they are said to be formed by adding K_4FeCy_6Aq to niobic acid in presence of KHC_2O_4: $Nb_{16}K(FeCy_6)_2.67H_2O$ (?); $Nb_{12}K_2.FeCy_6.39H_2O$ (?); $(NbO)_5K_9(FeCy_6)_6.10H_2O$ (?).

Potassium ferrocyanide K_4FeCy_6. (*Yellow prussiate of potash. Ferroprussiate of potash.*) Discovered about 1750 by Macquer; obtained by him by boiling Prussian blue with potash. Berthollet showed that the iron in it was an essential part of the salt. H.F. $[K^4,Fe,Cy^6] = 367{,}200$; $[K^4FeCy^6,Aq] = 5{,}400$ (Berthelot, *C. R.* 91, 82).

Formation.—1. By fusing nitrogenous animal matter (horn, feathers, dried blood, leather-clippings, &c.) with K_2CO_3 and scrap iron, lixiviating with water, filtering, and crystallising; KCy is formed, and on addition of water this reacts with the iron to produce K_4FeCy_6 (Liebig, *A.* 38, 20; Nöllner, *A.* 108, 8; Hoffmann, *D. P. J.* 151, 63). [$2Fe + 12KCNAq + 4H_2O = 2K_4FeCy_6Aq + 4KOHAq + 2H_2$; or in presence of air $2Fe + 12KCNAq + 2H_2O + O_2 = 2K_4FeCy_6Aq + 4KOHAq$].—2. By heating $NH_4.SCN$ with scrap iron to dull redness, and dissolving out with water (Gélis, *W. J.* 1862. 283; 1863. 321; Fleck, *W. J.* 1863. 323; Alander, *D. P. J.* 226, 318; Tscherniak a. Gunsburg, *J.* 1878. 1123).—3. By the action of KCNAq on $Fe(OH)_2$, $FeCO_3$, or FeS, &c. (Fresenius a. Haidlen, *A.* 43, 132; Liebig, *A.* 38, 20).—4. By reaction between KOHAq and various ferrocyanides.

Preparation.—*Pure* Prussian blue $Fe_4(FeCy_6)_3$ is added to boiling KOHAq so long as the blue colour changes to brown, the solution is filtered, evaporated, and the salt is recrystallised from water. Impure K_4FeCy_6 (prepared from commercial Prussian blue) generally contains K_2CO_3, K_2SO_4, &c., and sometimes Prussian green; it may be purified, according to Berzelius, by heating until it effloresces, and then to its melting-point, dissolving in water, filtering from C and Fe carbide, adding acetic acid to convert K_2CO_3 and KCy into acetate, adding Ba acetate little by little to pp. sulphates, filtering, evaporating, ppg. K_4FeCy_6 by alcohol, and recrystallising twice from water.

Properties.—Reddish-yellow quadratic pyramids (Bunsen, *P.* 36, 404); crystallises with $3H_2O$. S.G. 1·86 (*W. J.* 1875. 503). Not poisonous. Loses all H_2O at 60°–80°; unchanged at ordinary temperatures. Sol. c. 4 pts. cold H_2O and in c. 2 pts. at 100°; insol. alcohol; 1,000 c.c. K_4FeCy_6Aq saturated at 15° has S.G. 1·114, and contains 258·77 g. salt and 885·34 g. water (Michel a. Kraft, *A. Ch.* [3] 41, 471). Solution decomposed in sunlight with ppn. of Prussian blue and evolution of HCN.

Reactions.—1. *Heated in closed vessel* melts at little above red heat, evolves N, and leaves mixture of KCy and Fe carbide; if salt is not dehydrated it gives off CO_2, NH_3, HCN, and N.—2. *Heated to redness in air* gives KCyO; same product formed by heating with *reducible metallic oxides.*—3. Changed slowly by *ozone* into K_3FeCy_6; not, however, acted on by *oxygen.*—4. K_4FeCy_6Aq *electrolysed* forms K_3FeCy_6 at positive, and KOHAq and H at negative, pole (Schlagdenhauffen, *J.* 1863. 305).—5. K_4FeCy_6Aq is changed to K_3FeCy_6Aq by *oxidisers, e.g.* $KMnO_4Aq$, PbO_2, MnO_2 (Brodie, *P.* 120, 302; Weltzien, *A.* 138, 129; Reindel, *J. pr.* 76, 342; Bottger, *J. pr.* 76, 238; Braun, *J. pr.* 90, 356).—6. *Chlorine* forms KCl and K_3FeCy_6; *bromine* reacts similarly to Cl.—7. *Iodine* dissolves in warm K_4FeCy_6 to form an olive green liquid, from which crystals of a double compound of KI and K_3FeCy_6 $(KI.K_3FeCy_6)$ separate on cooling (Mohr, *A.* 105, 57; Blomstrand, *J. pr.* [2] 3, 207; Preuss, *A.* 29, 323).—8. Fairly conc. *nitric acid* forms *nitroprussic acid* (*q.v.* p. 341); very conc nitric acid decomposes the salt entirely, forming N, Cy, NO, CO_2, KNO_3, and Fe_2O_3.—9. Dilute *sulphuric acid* forms H_4FeCy_6Aq if cold, if the H_2SO_4Aq is warm HCy is evolved ($2K_4FeCy_6Aq + 3H_2SO_4Aq = 6HCyAq + FeK_2(FeCy_6) + 3K_2SO_4Aq$; Wittstein, *Vierteljahr. Pharm.* 4, 515; Aschoff, *Ar. Ph.* [2] 106, 257). Heated with conc. H_2SO_4 almost pure CO is evolved (Fownes, *P. M.* [3] 21, 21) [$K_4FeCy_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO$].—10. Decomposed by boiling with *mercuric oxide* and water, $HgCy_2$ and $Fe_2(OH)_6$ being formed (Weith, *Z.* 1869. 381).—11. Boiled with *salammoniac* NH_4Cy is volatilised (Wyrubow, *A. Ch.* [4] 16, 280).—12. *Ammoniacal silver nitrate* forms $Fe(OH)_3$ and AgCy.KCy.—13. K_4FeCy_6 boiled with a very little *ferric chloride solution* forms some K_3FeCy_6 (Williamson, *A.* 57, 238).—14. K_4FeCy_6Aq reacts with most metallic salts to give pps. of *ferrocyanides* (*q.v.*).

Double ferrocyanides derived from potassium ferrocyanide. (Those only are mentioned here which contain potassium, and another metal the first letter of the name of which follows P in alphabetical order; the other double ferrocyanides containing K are mentioned under the headings of the metal other than K).

$Na_3K.FeCy_6.9H_2O$ (Wyrubow, *A. Ch.* [4] 16, 280).

$Na_2K_2.FeCy_6.8H_2O$ (Reindel, *J. pr.* 100, 6).

$NaK_3.FeCy_6.3H_2O$ (Reindel, *J. pr.* 65, 450).

$K_2Sr.FeCy_6.3H_2O$ (Wyrubow, *A. Ch.* [4] 21, 271).

$K.W_2.FeCy_6.7H_2O$; $K_2W_5FeCy_6.20H_2O$ (?) (Wyrubow, *A. Ch.* [5] 8, 444).

$K_2U_3.FeCy_6.6H_2O$ (?); $K_23UO_2.(FeCy_6)_2.6H_2O$; $K_65UO_2(FeCy_6)_4.12H_2O$ (W., *l.c.*; Atterberg, *Bl.* [2] 241, 355).

$K_{18}V.(FeCy_6)_6$ (??) (W., *l.c.*);
$K_6(VO)_5(FeCy_6)_4.60H_2O$ (?) (A., *l.c.*).

$KY.FeCy_6$ (Clève a. Hoeglund, *Bl.* [2] 18, 197).

Double salts containing potassium ferrocyanide.

$K_4FeCy_6.2KNO_3.2NaNO_3$ (Martius, *Z.* 1866. 319; *cf.* Wyrubow, *A. Ch.* [4] 16, 280).

$K_4FeCy_6.3HgCy_2.4H_2O$ (Kane, *A.* 35, 357; Löwe, *J.* 1857. 273).

Osmium ferrocyanide Os_2FeCy_6 (Martius, *A.* 117, 357).

Rubidium ferrocyanide $Rb_4FeCy_6.2H_2O$. Yellow triclinic crystals. Obtained by dissolving Rb_2CO_3 in H_4FeCy_6Aq, and evaporating (Piccard, *J. pr.* 86, 449).

Silver ferrocyanide Ag_4FeCy_6 (Glassford a. Napier, *P. M.* [3] 25, 71); with $2H_2O$, according to Wyrubow (*A. Ch* [5] 8, 444). White pp. turning blue in the air by adding K_4FeCy_6Aq to solution of a Ag salt. Sol. in KCyAq. Combines with NH_3 to form

$$Ag_4FeCy_6.2NH_3.6H_2O$$

(Gintl, *W. A. B.* 59, 551; 60, 470). Decomposed by warm NH_3Aq to $FeO.xH_2O$ and solution of AgCy and NH_4Cy (Weith, *Z.* [2] 5, 381).

Sodium ferrocyanide $Na_4FeCy_6.12H_2O$ (Berzelius), or $9H_2O$ when ppd. by addition of alcohol to its hot solution (Weith, *A.* 147, 329). Obtained by boiling Prussian blue with NaOHAq, filtering, and cooling. Monoclinic, pale-yellow crystals, which effloresce in air (Reindel, *J. pr.* 102, 42).

Strontium ferrocyanide $Sr_2FeCy_6.15H_2O$; easily soluble, yellow monoclinic crystals. Obtained by dissolving $SrCO_3$ in H_4FeCy_6Aq, evaporating, and recrystallising the crystals which separate (Bette, *A.* 22, 148). Wyrubow (*A. Ch.* [4] 16, 280) obtained crystals with $8H_2O$.

Thallium ferrocyanide $Tl_4FeCy_6.2H_2O$; small, lustrous, yellow triclinic crystals. Formed by crystallising a mixed solution of conc. K_4FeCy_6 with conc. Tl_2CO_3Aq (Lamy a. Descloiseaux, *A. Ch.* [4] 17, 310; Wyrubow, *A. Ch.* [4] 16, 280).

Tin ferrocyanides. *Stannous ferrocyanide* $Sn_2FeCy_6.4H_2O$; white pp. by adding K_4FeCy_6 to $SnCl_2$ solution (Wyrubow, *A. Ch.* [5] 8, 444). *Stannic ferrocyanide* $SnFeCy_6.4H_2O$; brownish pp. by adding K_4FeCy_6Aq to $SnCl_4$ solution (W., *l.c.*). Wyrubow describes other ferrocyanides of tin, but their composition is doubtful.

Titanium ferrocyanides. According to Wyrubow (*A. Ch.* [5] 8, 444) various Ti ferrocyanides are obtained by adding K_4FeCy_6Aq to solutions of Ti salts; the composition of these compounds is doubtful (*cf.* Atterberg, *Bl.* [2] 24, 355).

Thorium ferrocyanide $Th_2FeCy_6.4H_2O$ (Clève, *Bl.* [2] 21, 119).

Uranium ferrocyanide $UFeCy_6.10H_2O$; $U_3K_2FeCy_6.20H_2O$ (Wyrubow, *A. Ch.* [5] 8, 444).

Vanadium ferrocyanide. The salt $(VO)_2FeCy_6.11H_2O$ is said to be formed by ppg. V salts by K_4FeCy_6Aq (Atterberg, *Bl.* [2] 24, 355).

Yttrium ferrocyanide. The salt Y_2FeCy_6 is said to be produced by boiling yttria with Prussian blue, filtering and evaporating slowly (Popp, *A* 131, 179). For double K-Y salt *v. Potassium ferrocyanide.*

Zinc ferrocyanide $Zn_2FeCy_6.3H_2O$ (Schindler, *Magaz. Pharm.* 35, 71), or with $4H_2O$ (Wyrubow, *A. Ch.* [5] 8, 444). White pp. by adding excess of $ZnSO_4Aq$ to K_4FeCy_6Aq; or, better, by using H_4FeCy_6. If the $ZnSO_4Aq$ contains NH_3, a *double salt*, $Zn_2FeCy_6.3NH_3.H_2O$, is produced (Bunsen, *P.* 34, 134; Mouthiers, *A.* 64, 297).

FERRICYANHYDRIC ACID AND FERRICYANIDES.

Ferricyanhydric acid H_4FeCy_6. (*Ferricyanic acid. Hydroferricyanic acid. Ferriprussic acid. Hydrogen ferricyanide.*) Prepared by decomposing $Pb_3(FeCy_6)_2$ by dilute H_2SO_4Aq (Gmelin); or, preferably, by adding to cold conc. K_3FeCy_6Aq two or three times its volume of very conc. HClAq, and collecting the acid which separates on a porous plate, and drying *in vacuo* (Schafarik, *W. A. B.* 47, 262). Forms lustrous brownish-green needles; very sol. in water and alcohol, insol. in ether; decomposed in air with evolution of HCN and production of blue-coloured residue (Posselt, *A.* 42, 163). Joannis (*C. R.* 94, 449, 511, 725) examined the thermal data for H_3FeCy_6Aq; the solution was prepared by the action of Br on H_4FeCy_6Aq:—

$[H^3FeCy^6Aq, 3KOHAq] = 43,500$; $[H^3, Fe, Cy^6, Aq] = 77,400$ (gaseous Cy); $[H^3FeCy^6Aq, H] = 29,200$ (production of solution of H_4FeCy_6 from solution of H_3FeCy_6).

Ferricyanides (*Ferriprussiates*). *Salts of ferricyanhydric acid.* These salts are produced by the action of oxidising agents on the ferrocyanides; the action consists in the withdrawal of ¼ of the metal of the ferrocyanide; $M_4FeCy_6 - M = M_3FeCy_6$. Alkali ferricyanides are soluble in water; most of the other ferricyanides are insoluble, and may be formed by ppn. Alkali ferricyanides give pps. with salts of many different metals.

Ammonium ferricyanide $(NH_4)_3FeCy_6.3H_2O$. Chlorine is passed into NH_4 ferrocyanide solution until the liquid ceases to give a blue pp. or colour with $FeCl_3Aq$ (free from $FeCl_2$); the liquid is evaporated slowly, then cooled; the crystals of $(NH_4)_3FeCy_6$ are separated from those of NH_4Cl formed in the reaction, and are recrystallised from water. Cannot be wholly dehydrated without partial decomposition, HCN being evolved and some Prussian blue produced (Jacquemin, *Bl.* [2] 1, 319; Bette, *A.* 23, 115).

By boiling K_4FeCy_6Aq with $(NH_4)_2SO_4Aq$ Schaller (*Bl.* [2] 1, 275; 2, 93) obtained crystals of the *double salt* $(NH_4)_2K.FeCy_6$. Schuler (*W. A. B.* 77, 692) obtained the *double salt* $NH_4Pb.FeCy_6.3H_2O$.

Barium ferricyanide $Ba_3(FeCy_6)_2 20H_2O$ (Schuler, *W. A. B.* 77, 692). By passing Cl into a solution of $BaK_2.FeCy_6$ (obtained by mixing conc. $BaCl_2Aq$ with excess of conc. K_4FeCy_6Aq), warming to remove excess of Cl, adding alcohol, and cooling, the *double salt* $BaK.FeCy_6.3H_2O$ was obtained (Bette, *A.* 23, 115).

Beryllium ferricyanide (Joczynsky, *Z.* 1871. 276). Composition undecided.

Bismuth ferricyanide $Bi_3(FeCy_6)_6$. Brownish red pp. produced by adding K_3FeCy_6Aq to $Bi(NO_3)_3$ dissolved in very little HNO_3Aq, washing with cold water, and drying *in vacuo* over H_2SO_4. Decomposed by boiling water with evolution of HCN. Cl, in presence of hot water, forms Bi_2O_3, Prussian blue, and HCN; Br and NaOHAq gives Bi_2O_3 and Fe_2O_3. Reduced by Na-amalgam to $Bi_4(FeCy_6)_5$.

Also obtained by reaction of dilute HNO_3Aq with $Bi_4(FeCy_6)_5$ (*q. v.*) (Pattison Muir, *C. J.* [2] 16, 654; 17, 40).

Cadmium ferricyanide. Yellow pp. obtained by adding K_3FeCy_6Aq to solution of a Cd salt; composition undecided. This pp. dissolves in NH_3Aq; if little NH_3Aq is used the *double salt* $Cd_3(FeCy_6)_26NH_3.3H_2O$ is formed; if much NH_3Aq is added the salt $Cd_3(FeCy_6)_2.4NH_3.2H_2O$ is produced after a time (Wyrubow, *A. Ch.* [5] 10, 413).

Calcium ferricyanide $Ca_3(FeCy_6)_2.10$ (or 12) H_2O (Berzelius, *S.* 30, 12; Bette, *A.* 23, 115). Formed by the action of Cl on Ca_2FeCy_6Aq. Fine, red, deliquescent needles. The double salt $CaK.FeCy_6$ is described by Mosander (*P.* 25, 390).

Cerium ferricyanide $CeFeCy_6.4H_2O$ (Jolin, *Bl.* [2] 21, 535). By adding alcohol to a mixture of Ce nitrate with K_3FeCy_6Aq.

Chromium ferricyanide. Compound obtained by adding K_3FeCy_6 to a Cr salt. Composition undecided (*v.* Stridsberg, *J.* 1864. 301). Christensen (*J. pr.* [2] 23, 49) describes the *double compound* $CrFeCy_6.5NH_3.1\frac{1}{2}H_2O$.

Cobalt ferricyanide $Co_3(FeCy_6)_2$. Red-brown pp. obtained by adding K_3FeCy_6Aq to a Co salt (*Gm.* 7, 497). When $Co_3(FeCy_6)_2$ is kept in contact with NH_3Aq for a long time the *double compound* $Co_3(FeCy_6)_2.2NH_3.6H_2O$ is produced (Braun, *A.* 125, 153, 197).

Copper ferricyanides; *Cuprous ferricyanide* $Cu_3(FeCy_6)$; brownish red pp. formed by adding Cu_2Cl_2 in HClAq to K_3FeCy_6Aq. Sol. in NH_3Aq, but not in NH_4 salt solution. *Cupric ferricyanide* $Cu_3(FeCy_6)_2$; yellowish pp. formed when a cupric salt solution is ppd. by K_3FeCy_6; said always to contain excess of K_3FeCy_6, possibly in combination; sol. NH_3Aq, also in solutions of NH_4 salts (Wittstein, *R. P.* 63, 314; Williamson, *A.* 57, 225).

Iron ferricyanides. Turnbull's blue, Fe_5Cy_{12}, is probably *ferrous ferricyanide* $Fe_3(FeCy_6)_2$. *Soluble Prussian blue*, KFe_2Cy_6, is probably *potassium-ferrous ferricyanide*, $FeK.FeCy_6$: there is also a corresponding NH_4 salt. *Pelouze's green* (or Prussian green), $Fe_{13}Cy_{36}$, may be regarded as *ferroso-ferric ferricyanide*, $Fe^{II}_3.Fe^{III}_4(FeCy_6)_6$.

Addition of $FeCl_3Aq$ to K_4FeCy_6Aq produces soluble Prussian blue, which is generally regarded as a ferricyanide; the same compound is produced by adding $FeSO_4Aq$ to K_3FeCy_6Aq. The formation of a ferricyanide from the reaction between a ferrous salt and a ferricyanide, and also from that between a ferric salt and a ferrocyanide, is explained by Skraup's observation, that ferrous salts reduce ferricyanides to ferrocyanides, while ferric salts oxidise ferro- to ferri- cyanides (*W. A. B.* [*Juniheft*, 1876] vol. 74, part 2). When soluble Prussian blue is treated with $FeSO_4Aq$ Turnbull's blue, $Fe_3(FeCy_6)_2$, is formed; when ferric sulphate is used the product is Prussian blue, which is ferric ferrocyanide $Fe_4(FeCy_6)_3$. Ferrous ferrocyanide $Fe_2.FeCy_6$ (*q.v.* p. 334), when partially oxidised, produces ferrous ferricyanide (Turnbull's blue), and when more fully oxidised ferric ferrocyanide (Prussian blue) is formed. These reactions suffice to show how easy is the passage from ferrocyanides of iron (both ferrous and ferric salts) to ferricyanides, and *vice versâ*.

Ferrous ferricyanide $Fe_3(FeCy_6)_2$. (*Turnbull's blue*). Obtained by adding K_3FeCy_6Aq to an excess of a ferrous salt, digesting the pp. for some time with the ferrous solution, and washing with hot water; also obtained by partial oxidation of ferrous ferrocyanide $Fe_2.FeCy_6$, which is the pp. formed by adding H_4FeCy_6Aq to a ferrous salt. Best prepared by ppg. excess of a ferrous salt by H_3FeCy_6Aq (*q. v.*). When dried in air retains about 28 p.c. water (Williamson, *A.* 57, 225); cannot be completely dehydrated without partial decomposition, giving Fe_2O_3 and Prussian blue, $Fe_4(FeCy_6)_3$. Oxidises when moist by exposure to air to ferric ferrocyanide (*Prussian blue*). Deep-blue powder, with tinge of copper-red; insol. water, alcohol, and dilute mineral acids; sol. $H_2C_2O_4Aq$. Decomposed by KOHAq or K_2CO_3Aq, giving K_4FeCy_6Aq and Fe_3O_4; Prussian blue gives Fe_2O_3 and K_4FeCy_6Aq.

Ferroso-ferric ferricyanide $Fe^{III}_4.Fe^{II}_3(FeCy_6)_6 = Fe_{13}Cy_{36}$. (*Prussian green. Pelouze's green*) (Pelouze, *A. Ch.* [2] 69, 40; Erlenmeyer, *Lehrb. der organ. Chemie* [1867], p. 48 *et seq.*; Williamson, *A.* 57, 225). Green pp obtained by passing excess of Cl into K_4FeCy_6 or K_3FeCy_6, boiling the liquid, washing the pp. with conc. boiling HClAq (to remove Fe_2O_3 and Prussian blue) so long as the liquid is turned blue on addition of water, washing with water, and drying. Also produced by prolonged contact of K_4FeCy_6 with aqueous acids; and by boiling soluble Prussian blue (K-ferrous ferricyanide, $FeK.FeCy_6$) with HNO_3Aq. Changed to Prussian blue, $Fe_4(FeCy_6)_3$, by prolonged contact with air. Heated to 180° gives off Cy and HCy. Decomposed by KOHAq, giving $Fe_2O_6H_6$ and K_4FeCy_6Aq and K_3FeCy_6.

Another cyanide of iron, which is probably a ferroso-ferric ferricyanide, *viz.* $Fe_3C_{18} = Fe_3{}^{II}Fe_2{}^{III}(FeCy_6)_4$, is described by Reynolds (*C. J. Trans.* 1888. 767) as a black solid, formed by heating to boiling 40 parts of bromine with 20 parts of K_3FeCy_6 in saturated solution in a flask with a reversed condenser for 5 or 6 hours, washing with dilute HClAq, then thoroughly with cold water, and drying over H_2SO_4 *in vacuo*. The substance is hygroscopic; potash decomposes it to FeO_3H_3, K_4FeCy_6, and K_3FeCy_6; it dissolves in conc. HClAq after long digestion, giving $FeCl_2$ and $FeCl_3$; when moist it is changed in air to Prussian blue.

Double ferricyanides derived from ferrous ferricyanides.

Ammonium-ferrous ferricyanide $NH_4Fe.FeCy_6.1\frac{1}{2}H_2O$ (Wyrubow, *A. Ch.* [5] 8, 444). Corresponds with, and prepared in manner similar to, the K salt (*v. post*), but more stable than that salt; may be dried without decomposition; not ppd. from solutions by alcohol.

Potassium-ferrous ferricyanide $KFe^{II}.FeCy_6$. (*Soluble Prussian blue.*) This salt may perhaps be better regarded as potassium-ferric ferrocyanide $KFe^{III}.FeCy_6$. It is obtained by mixing $FeCl_3Aq$ and K_4FeCy_6Aq in the ratio $FeCl_3:K_4FeCy_6$; solutions of known strength of the reacting salts are poured simultaneously into the same vessel with constant stirring, the pp. is at once washed with cold water, and dried over H_2SO_4 *in vacuo* (Skraup, *W. A. B.* [*Juniheft*, 1876] 74, 2nd part). It is also formed by dissolving about 80 g. K_3FeCy_6 in water, and adding about 3 g. $FeSO_4.7H_2O$, free from ferric salt, dissolved in water; the pp. is washed with air-free water containing a little KCl, and then with pure water (Skraup, *l.c.*). Dried *in vacuo* the salt has the composition $2(KFe.FeCy_6).3\frac{1}{2}H_2O$ (Skraup, *l.c.*). (For preparation *v.* also Brücke, *J.* 1866. 288; Reindel, *D. P. J.* 190, 396).

A blue solid, sol. cold water, solution is decomposed by boiling with formation of yellowish pp. Addition of salts, mineral acids, or alcohol, to the aqueous solution of this compound produces a blue pp. After continued washing with alcohol, soluble blue becomes insol. in water (Skraup, *A.* 186, 371). From an aqueous solution of soluble blue, containing a little alkali, ferric salts ppt. Prussian blue, $Fe_4(FeCy_6)_3$, and ferrous salts ppt. Turnbull's blue $Fe_3(FeCy_6)_2$ (Skraup, *l.c.*). Alkalis, NH_3Aq, and alkali carbonates ppt. $Fe_2O_6H_6$, and form a solution of ferrocyanide. Digested with K_4FeCy_6Aq, K_3FeCy_6, and potassium ferrous ferrocyanide ($K_2Fe.FeCy_6$) are produced.

The blue compound obtained by Williamson (*A.* 57, 225) by heating potassium ferrous ferrocyanide, $K_2Fe^{II}.FeCy_6$, with dilute HNO_3Aq appears to be identical with soluble Prussian blue. This body was prepared by digesting 1 pt. white $K_2Fe^{II}.FeCy_6$ with 1 pt. conc. acid and 20 pts. water; when the liquid was nearly boiling NO escaped, and the lamp was removed; treatment with HNO_3Aq was continued until a sample of the blue compound produced gave pure $Fe_2O_6H_6$, unmixed with Fe_3O_4, when decomposed by KOHAq.

Lead ferricyanide. Gmelin gives the formula $Pb_3(FeCy_6)_2$; Schuler (*W. A. B.* 77, 692) gave $Pb_3(FeCy_6)_2.4H_2O$; v Zepharovich (*W. A. B.* 59 [2nd part], 800) $Pb_3(FeCy_6)_2.16H_2O$. According to Wyrubow (*A. Ch.* [5] 10, 413) the salt with $16H_2O$ is obtained by mixing hot solutions of equivalent weights of $Pb(NO_3)_2$ and K_4FeCy_6, and allowing to cool. Small dark-reddish crystals; not e. sol. water. *Double salts*; $PbK.FeCy_6.3H_2O$ (Wyrubow, *l.c.*). The mother-liquor from $Pb_3(FeCy_6)_2$ deposits this salt on cooling. Red, six-sided triclinic plates; *a*:*b*:*c* =1·7205:1:·9309. Decomposes on exposure to air. $Pb_3(FeCy_6)_2.3PbO_2H_2.11H_2O$; $Pb_3(FeCy_6)_2.Pb(NO_3)_2.12H_2O$ (Schuler, *W. A. B.* 77, 692).

Magnesium ferricyanide $Mg_3(FeCy_6)_2$; reddish brown, non-crystallisable; obtained by treating Mg_2FeCy_6 (*q. v.*) with Cl (Bette, *A.* 23, 115). Reindel (*J. pr.* 103, 166) obtained the *double salt* $MgK.FeCy_6$.

Manganese ferricyanide $Mn_3(FeCy_6)_2$; brownish pp. by adding K_3FeCy_6Aq to solution of a Mn salt (Wittstein, *R. P.* 63, 314).

Nickel ferricyanide; pp. formed by adding K_3FeCy_6Aq to solution of a Ni salt is probably $Ni_3(FeCy_6)_2$ (*Gm.* 7, 500). According to Reynoso (*A. Ch.* [3] 30, 252) addition of K_3FeCy_6Aq to an ammoniacal solution of a Ni salt produces a yellow pp. of the *double salt* $Ni_3(FeCy_6)_2.4NH_3.H_2O$.

Potassium ferricyanide K_3FeCy_6. (*Red prussiate of potash*).

Formation. — 1. By adding PbO_2 to K_4FeCy_6Aq, and neutralising the KOH produced by an acid (Seuberlich, *D. P. J.* 238, 484).—2. By adding BrAq to K_4FeCy_6Aq until $FeCl_3Aq$ ceases to give blue pp.—3. By passing ozonised O into K_4FeCy_6Aq. — 4. By electrolysing K_4FeCy_6Aq (Schlagdenhauffen, *J.* 1863. 305).

Preparation.—1. K_4FeCy_6Aq is digested with potassium-ferrous ferrocyanide, $K_2Fe.FeCy_6$ (*q.v.* p. 334) the liquid is filtered and crystallised (Williamson, *A.* 57, 225).—2. Well washed Cl is passed into cold K_4FeCy_6Aq, with constant agitation, until a few drops of the liquid give a brown-red colour, but no pp., with $FeCl_3Aq$; the liquid is evaporated, and the crystals are repeatedly recrystallised from water [$K_4FeCy_6Aq + Cl = KClAq + K_3FeCy_6Aq$] (Gmelin, *S.* 34, 325; Zimmermann, *D. P. J.* 127, 211). If the passage of Cl is continued too long some *Prussian green* is formed (*v. Ferroso-ferric ferricyanide*, p. 338). to remove this, Posselt (*A.* 42, 170) evaporates to the crystallising point, then adds 2 or 3 drops of KOHAq (not more), filters from $Fe_2O_6H_6$, and allows the liquid to crystallise. — 3. Rhien (*D. P. J.* 206, 151) recommends to mix HClAq with cold K_4FeCy_6Aq in the ratio $2K_4FeCy_6:HCl$, and then to add a cold filtered solution of bleaching powder until $FeCl_3Aq$ gives no blue pp.; any excess of acid is then neutralised by $CaCO_3$, and the solution is evaporated to the crystallising point. The first crop of crystals is pure, the subsequent crops contain traces of lime which may be removed by re-crystallisation.

Properties—Large red prismatic crystals; monoclinic, *a*:*b*:*c* = ·7457:1:·5985 (Kopp, *Krystallographie*, 311); according to Schabus (*W. A. B.* 1850. 582) the crystals are trimetric with the ratio of axes *a*:*b*:*c* = 1·2418:1·6706:1. S.G. 1·8 1·85 (Schabus, *l.c.*; Wallace, *C. J.* 7, 77). S. 33 at 4·5°, 36·6 at 10°, 39·4 at 15·5°, 58·7 at 38°, 77·5 at 100°, 81·9 at 104° (=B.P. of saturated solution) (Wallace, *l.c.*). S.G. of K_3FeCy_6Aq saturated at 15·5° = 1·178 (Schiff, *A.* 113, 199). Nearly insol. alcohol. H.F. [K^3, Fe, Cy^6] = 278,700; data obtained by oxidising K_4FeCy_6Aq by Cl and Br, also H_4FeCy_6Aq by Br, and reducing $Zn_3(FeCy_6)_2$ by HIAq (Joannis, *C. R.* 94. 449, 541, 725).

Reactions.—1. *Heated in a closed vessel*, decrepitates, evolves Cy and a little N, residue consists of KCy, K_4FeCy_6, $Fe_4(FeCy_6)_3$, C, Fe, and probably paracyanogen. *Heated in air*, Cy is evolved and Fe_2O_3 and KCy remain.—2. K_3FeCy_6Aq is *reduced* to K_4FeCy_6Aq by the action of sunlight (not by yellow light) (Vogel, *B.* 4, 90; Schönbein, *P.* 67, 87); also reduced by H_2S (Williamson, *A.* 57, 225); by alkali sulphide (Liesching, *D. P. J.* 128, 206); by thiosulphates (Diehl, *J. pr.* 79, 430; *cf.* Löwe, *J.* 1857. 273); by HI (Lenssen, *A.* 91, 240); by reduced Ag, Zn, Fe, Bi, &c. (Eder, *J. pr.* [2] 16, 211; Böttger, *C. C.* 1872. 708); by ferrous salts when hot (Skraup

A. 186, 371); by H_2O_2Aq in alkaline solution (Weltzien, *A.* 138, 129); also by SO_2Aq, phosphites and hypophosphites; also by many organic reducing agents, *e.g.* formic acid (Schönbein, *P.* 67, 87).—3. Alkaline solution of K_3FeCy_6 acts as an *oxidiser*, *e.g.*, towards sugar, starch, alcohol, oxalic acid (Wallace, *C. J.* 7, 77), indigo (Mercer, *P. M.* [3] 31, 126); NO is oxidised to HNO_3, P to H_3PO_4, and S is said to be oxidised to H_2SO_4Aq (Wallace, *l.c.*).—4. *Ammonia* reacts with K_3FeCy_6Aq to form K_4FeCy_6, $(NH_4)_4FeCy_6$, and N (Mouthiers, *J. Ph.* [3] 11, 254).—5. *Potash* when boiled down with conc. K_3FeCy_6Aq produces K_4FeCy_6 and KCy, evolving Cy and ppg. Fe_2O_3 (Boudault, *J. Ph.* [3] 7, 437). 6. Some *oxidisable metallic oxides*, *e.g.* PbO, Cr_2O_3, MnO, SnO, when boiled with K_3FeCy_6Aq in presence of KOH, form K_4FeCy_6Aq, and a higher oxide of the metal; CoO and NiO are not thus oxidised; salts of Ag and Au produce Fe_2O_3 with solution of K_4FeCy_6 and double cyanide of K and Ag, or K and Au.—7. When *mercuric oxide* is boiled with K_3FeCy_6Aq, $HgCy_2Aq$ is formed, and the whole of the Fe is ppd. as Fe_2O_3 (Gmelin).—8. K_3FeCy_6Aq is decomposed by excess of *chlorine* with production of HCy and CyCl; on boiling, or on addition of alkali, the liquid deposits *ferroso-ferric ferricyanide* $Fe_4^{III}.Fe_3^{II}(FeCy_6)_6$ (*q. v.* p. 338). Bromine, in excess, and with prolonged action, produces Prussian blue; when the action is continued for a shorter time a black cyanide of Fe, Fe_7Cy_{18}, probably a ferroso-ferric compound $Fe_3^{II}Fe_2^{III}(FeCy_6)_3$, is formed (*v.* p. 338); when the ferricyanide is in excess Turnbull's blue is produced (Reynolds, *C. J. Trans.* 1888. 767).—9. *Nitric acid* produces nitroprusside of potassium (*q. v.* p. 341) and nitre (Playfair, *P. M.* [3] 26, 197, 271, 348).—10. *Hydrochloric acid* when boiled with K_3FeCy_6 forms KCl, $FeCl_2$, and *Turnbull's blue*, $Fe_3(FeCy_6)_2$. 11. *Nitric oxide* produces K nitroprusside (Bunge, *Z.* 1866. 82).

Combination.—With *potassium iodide* to form $K_3FeCy_6.KI$; very unstable salt (Preuss, *A.* 29, 323; Mohr, *A.* 105, 57; Blomstrand, *J. pr.* [2] 3, 207; *cf.* Kern, *C. N.* 33, 184).

The *double salts* $KNa_2.FeCy_6$, $K_3Na_3(FeCy_6)_2$, $K_2NaFeCy_6$, have been isolated (*v.* Reindel, *J. pr.* 102, 43; *ibid. Z.* 1870. 147; Laurent, *J.* 1849. 291; Wyrubow, *Bl.* [2] 12, 98; 14, 145).

Silver ferricyanide Ag_3FeCy_6. Orange yellow salt obtained by adding K_3FeCy_6Aq to $AgNO_3Aq$. When freshly ppd. Ag_3FeCy_6 is treated with NH_3Aq, or when K_3FeCy_6Aq is added to $AgNO_3Aq$ with enough NH_3Aq to form a clear liquid, a reddish pp. of the *double salt* $2Ag_3FeCy_6.3NH_3.\frac{1}{2}H_2O$ is produced (Gintl, *W.A.B.* 59, 554). This compound dissolves in excess of NH_3Aq, and on heating decomposes, giving $(NH_4)_4FeCy_6Aq$, NH_3Aq, Ag_4FeCy_6, and N.

Sodium ferricyanide $Na_3FeCy_6.H_2O$. Ruby-coloured deliquescent prisms; obtained by oxidising Na_4FeCy_6Aq by Cl and evaporating. S. 18·9 cold water, 80 at 100° (Bette, *A.* 23, 115; Reindel, *J. pr.* 102, 43; Kramer, *J. Ph.* 15, 98).

Tin ferricyanides; *stannous ferricyanide* $Sn_3(FeCy_6)_2$, gelatinous pp. by adding K_3FeCy_6Aq to $SnCl_2$ solution. Wyrubow (*A.Ch.* [5] 8, 414) gives the formula $Sn_9(FeCy_6)_4.25H_2O$.

Ferricyanides **of** *uranium*, *vanadium*, **and** *zinc* **probably exist, but there is little accurate knowledge regarding them.**

NITROPRUSSIDES (*Nitroprussiates. Nitroferricyanides.*) Salts of *nitroprussic acid* $H_2FeC_5N_6O$ (probably $H_2FeCy_5.NO$). These salts were discovered by Playfair in 1850 (*P. M.* [3] 36, 197, 271, 348). They have been studied by Gerhardt, Hadow, Roussin, and others, but their constitution cannot be regarded as finally determined. The nitroprussides are formed by reactions between nitric acid and the alkali ferro- or ferri-cyanides, or between ferro- or ferri-cyanhydric acid and nitric oxide, or by adding KNO_2 and a dilute acid to a ferrocyanide. The first products of the reaction between K_4FeCy_6Aq and HNO_3 are K_3FeCy_6 and NO; these then react to produce K nitroprusside with evolution of HCy, N, and CO_2. According to Jensen (*J. Ph.* [5] 11, 315) continued electrolysis of K_3FeCy_6 produces a liquid which gives the reactions of K nitroprusside. By boiling a mixture of $FeCl_3Aq$ and KCy, to which KNO_2 has been added, K nitroprusside is formed; according to Roussin (*A.Ch.* [3] 52, 285) this process is analogous to that whereby *iron nitrosulphide* (*q. v.* under IRON) is produced, K_2S being used in place of KCy. Alkali nitroprussides are soluble in water; the insoluble salts, *e.g.* of Cu, Fe, Zn, are obtained from these by double decomposition; the Fe or Cu salt decomposed by NH_3Aq, CaOAq, or BaOAq, gives a solution of the NH_4, Ca, or Ba nitroprusside. The nitroprussides are generally coloured and crystallise well. A solution of a nitroprusside gives a deep brilliant purple colour with an alkali sulphide; the colour soon fades; this reaction is used as a very delicate test for nitroprussides. The nitroprussides are decomposed by boiling with alkalis, giving Fe_2O_3, N, alkali ferrocyanide, and probably alkali nitrite. With H_2S they give Fe_2O_3, Prussian blue, S, a ferrocyanide, and a nitrosulphide of Fe; they are not usually changed by SO_2, sulphites, or thiosulphates, but are decomposed by hot conc. H_2SO_4. Some of these salts are stable; others undergo change in solution with ppn. of Prussian blue or Fe_2O_3.

The constitution assigned by Gerhardt to the nitroprussides (*Traité*, 1, 344) was $M_2FeCy_5.NO$ $[M = K, \frac{Ca}{2}$, &c.] which represents the compounds as salts of a dibasic acid containing the groups NO and Cy in combination with Fe. The reaction between ferricyanhydric acid and nitric oxide is represented thus: $H_3FeCy_6 + NO = H_2FeCy_5.NO + HCy$. Hadow (*C. J.* [2] 4, 341) supposed that the nitroprussides contained the group N_2O_3, because NO_2 does not change K_4FeCy_6Aq acidulated with H_2SO_4, whereas nitroprusside is formed by passing the gas evolved by heating starch with nitric acid into K_4FeCy_6Aq. Stadeler (*Z.* 5, 559) represents the preparation of K nitroprusside by the action of nitric acid on K_4FeCy_6 (Playfair's method) by the following equations (supposing that H_4FeCy_6 is first formed) (1) $2H_4FeCy_6Aq + HNO_3$

$$= 2H_3FeCy_6Aq + HNO_2Aq + H_2O;$$

$$(2)\ 2H_3FeCy_6Aq + 2HNO_2$$

$$= 2H_2FeCy_5(NO) + 2H_2O + Cy_2.$$

Regarding constitution of nitroprussides **v. Kyd (*A.* 74, 340), Weith (*Z.* [2] 4, 104).**

Nitroprussic acid $H_2FeC_5N_6O.H_2O$; probably $H_2FeCy_5.NO.H_2O$ (*Nitroferricyanic acid. Nitroferricyanhydric acid.*) Obtained by decomposing the Ag salt by an equivalent quantity of HClAq, or the Ba salt by an equivalent of H_2SO_4Aq, filtering, and evaporating *in vacuo*. Dark red deliquescent crystals; very easily decomposed in solution with formation of HCy and Fe_2O_3 (Playfair, *l.c.*).

Ammonium nitroprusside $(NH_4)_2FeC_5N_6O$. Obtained by decomposing the Fe salt by NH_3Aq, filtering and evaporating gently. Very unstable; solution deposits Prussian blue when boiled (Playfair).

Barium nitroprusside $BaFeC_5N_6O.3H_2O$. Obtained similarly to the NH_4 salt. Dark red, very soluble, quadratic crystals; give off most of their H_2O at 100° (P.).

Calcium nitroprusside $CaFeC_5N_6O.4H_2O$; very soluble, easily decomposed, crystals (P.).

Copper nitroprusside $CuFeC_5N_6O.2H_2O$; greenish pp. becoming grey on exposure to light; produced by adding solution of the K or Na salt to solution of a Cu salt (P.).

Iron nitroprusside (*ferrous*). Yellowish pink pp. by adding $K_2FeC_5N_6OAq$ to a ferrous salt; ferric salts give no pp. Decomposed by alkalis. Probably $Fe.FeC_5N_6O$ (P.).

Potassium nitroprusside $K_2FeC_5N_6O.2H_2O$ (P.; also Enz, *Vierteljahr. Pharm.* 2, 239). Prepared similarly to the sodium salt (*q. v.*). Dark red monoclinic crystals. S. c. 100 at 16°; sol. alcohol. Very deliquescent; solution slowly deposits Prussian blue. The *basic salt* $K_2FeC_5N_6O.K_2O.H_2O$ is obtained by mixing a solution of the normal salt with twice its volume of alcohol, and then adding potash. Jensen (*J. Ph.* [5] 11, 315) prepared the salt by reacting on K_3FeCy_6 with Ca hypochlorite solution.

Silver nitroprusside $Ag_2FeC_5N_6O$. Flesh-coloured pp. obtained from the Na or K salt by adding $AgNO_3Aq$; insol. water, alcohol, or HNO_3Aq (P.).

Sodium nitroprusside $Na_2FeC_5N_6O.2H_2O$. The other nitroprussides are made from this salt.

Preparation.—Four parts powdered K_4FeCy_6 are mixed with c. 5½ parts nitric acid S.G. 1·36, the conc. acid being diluted with its own volume of water. The acid is poured on to the salt in one quantity; the lowering of temperature is sufficient to moderate the reaction. The salt dissolves forming a coffee-coloured liquid, and evolving CO_2, N, Cy, and HCy; the liquid is placed in a large flask, and warmed on the water-bath so long as gases are evolved, and until the liquid gives a dark green or slate-coloured pp., instead of a blue pp., with a ferrous salt; on cooling, crystals of KNO_3 mixed with a little oxamide are deposited; the mother-liquor is neutralised by Na_2CO_3 (if K_2CO_3 is used, K nitroprusside is obtained) and boiled; it is then filtered, and evaporated at c. 40°, or better *in vacuo*, until crystallisation begins on cooling; the KNO_3 separates, and the mother-liquor yields the nitroprusside which is purified by recrystallisation from water, the prismatic crystals which form being removed from the hot liquid, dissolved in a little hot water, and allowed to crystallise by cooling (in this way the KNO_3 is separated) (P.; *cf.* Weith, *A.* 147, 312; Overbeck, *Ar. Ph.* [2] 72, 270; Roussin, *J.* 1852. 438; Schafarik, *W. A. B.* 47, 262).

Properties and Reactions.—Large ruby-red triclinic prisms; non-deliquescent. S. c. 40 at 15°. Does not lose water at 100° (P.; also Rammelsberg, *P.* 87, 107). 1. Aqueous solution decomposes rapidly in *sunlight* or on *heating* with ppn. of Prussian blue (Roussin, *J.* 1863. 309). 2. *Electrolysis* also produces Prussian blue (Schlagdenhauffen, *J.* 1863. 305; Weith, *A.* 147, 312).—3. An *alkaline solution* acts as an energetic oxidiser (Städeler, *A.* 151, 1).—4. *Boiled with alkalis* $Fe_2O_6H_6$ is ppd., N evolved, and the solution contains a nitrite and a ferrocyanide.—5. *Sulphuretted hydrogen* ppts. S and Prussian blue, and Na_4FeCy_6 remains in solution.—6. *Sodium amalgam*, in presence of acetic acid, produces a yellow colour, and alcohol causes a pp. in this liquid (for details *v.* Weith, *A.* 147, 312). 7. Oxidised to $NaNO_3$ and Na_3FeCy_6 by *potassium permanganate* in alkaline solution (Weith, *l.c.*). 8. Decomposed by *chlorine* when heated with it, or when exposed to sunlight (Davy, *C. N.* 38, 105).—9. Decomposed by *bromine* at temperatures above 100° (Weith, *l.c.*).—10. Easily decomposed by conc. *sulphuric acid*.—11. With *soluble metallic sulphides*, including NH_4 sulphide, a deep purple colour is produced; the liquid soon becomes turbid, and ppts. S and Fe_2O_3, while $NaNO_2$, Na_4FeCy_6, and NaSCy remain in solution. If an alcoholic solution is used the coloured body separates in oily drops, which give a green powder when dried *in vacuo* (Playfair).

Zinc nitroprusside $ZnFeC_5N_6O$. Yellow-rose pp. by adding $K_2FeC_5N_6OAq$ to solution of a Zn salt.

PERFERROCYANIDES.—When K_4FeCy_6Aq is heated with I a greenish-brown liquid is formed, from which alcohol ppts. a crystalline salt; this salt dissolves in water forming a dark reddish violet liquid (Stadeler, *A.* 151, 1). The salt is better prepared by mixing powdered K_4FeCy_6 with $KClO_3$, adding HClAq, heating very gently, neutralising by Na_2CO_3 after disengagement of gas has ceased, evaporating, ppg. by alcohol, and again dissolving in water and ppg. by alcohol (Boug, *Bl.* [2] 24, 268; Skraup, *A.* 189, 368). The salt is nearly black; it dissolves in water, is deep violet; the compound is very unstable, soon giving off Cy; even in the dark it changes colour to greenish black, and then dissolves to form a green solution. Boiled with water it forms K_3FeCy_6Aq and $Fe_2(OH)_6$. An aqueous solution of this salt gives green pps. with many metallic salts; it acts as an energetic oxidiser. Nitric acid forms K nitroprusside, $K_2FeC_5N_6O$. The salt probably has the composition K_2FeCy_6; if this is established the relation of potassium perferricyanide to potassium ferricyanide is similar to that of the ferri- to the ferro-cyanide (K_2FeCy_6, K_3FeCy_6, K_4FeCy_6).

Lanthanum cyanide, $LaCy_3$ (Frerichs a. Smith, *A.* 191, 365). A gelatinous pp., formed by adding solution of $La_2(SO_4)_3$ to KCyAq; forms double cyanides, *e.g.* $2LaCy_3.3PtCy_2.18H_2O$.

Lead cyanides. No cyanide of Pb has been isolated. Pb salts are not ppd. by HCNAq; but if NH_3 is present a white pp. of *lead oxycyanide* $PbCy_2.2PbO$ is obtained (Erlenmeyer, *J. pr.* 48, 356; Kugler. *A.* 66, 63). KCyAq added to Pb salts gives a pp. insoluble in excess of KCy. Joannis (*C. R.* 93, 271) gives the thermal data [Pb, C^4N^4, 2PbO, H^2O] = 17,800 (formation of solid $PbCy_2.2PbO.H_2O$ from gaseous Cy_2 and other materials as solids). Rammelsberg (*P.* 42, 114) says that addition of $ZnCy_2.2KCyAq$ to solution of a lead salt ppts. $PbCy_2.ZnCy_2$. The chlorocyanide $2PbCy_2.PbCl_2$ is described by Thorp (*Am.* 10, 229) as obtained by digesting $PbCl_2$ with KCyAq.

Magnesium cyanide. Not isolated; solution of MgO in HCNAq soon decomposes with evolution of HCN (*v.* Schulz, *J. pr.* 68, 257).

Manganese cyanides. No simple cyanide of Mn has been certainly isolated (Eaton a. Fittig, *A.* 145, 157). Several compounds are known which are best regarded as salts of *manganocyanhydric acid* H_4MnCy_6, which acid has itself been isolated, and *manganicyanhydric acid* H_3MnCy_6.

Manganocyanhydric acid H_4MnCy_6. Obtained by decomposing the Pb salt by H_2S, filtering, and evaporating *in vacuo* over H_2SO_4; insol. in ether, sl. sol. in alcohol (Descamps, *A. Ch.* [5] 24, 178). The Pb salt is obtained by adding $Pb(C_2H_3O_2)_2Aq$ to a freshly-prepared solution of K_4MnCy_6, which is itself formed by adding 10 grams manganous acetate to 40-45 grams KCy in 100 c.c. almost boiling water, and then adding 15-20 grams KCy, and dissolving the crystals of K_4MnCy_6 (which separate on cooling) in water (Christensen, *J. pr.* [2] 31, 163).

Manganocyanides. $K_4MnCy_6.6H_2O$ (for preparation *v. supra*); deep-blue quadratic crystals; lose $6H_2O$ over H_2SO_4; may be crystallised unchanged from a little KCyAq (Eaton a. Fittig, *A.* 145, 157; Descamps, *A. Ch.* [5] 24, 178). Freshly-prepared solution of this salt gives pps. with most metallic salts; the following are soluble in water and crystallisable:—Ba_2MnCy_6; BaK_2MnCy_6; Ca_2MnCy_6; $Na_4MnCy_6.16H_2O$; Sr_2MnCy_6 (E. a. F., *l.c.*; D., *l.c.*). Addition of I to K_4MnCy_6Aq ppts. all Mn as hydroxide (Beilstein a. Jawein, *B.* 12, 1528). According to Descamps (*A. Ch.* [5] 24, 178) passage of NO into manganocyanides produces salts analogous to *nitroprussides* (*q. v.* p. 340).

Manganicyanides. K_3MnCy_6 is obtained by allowing solution of K_4MnCy_6 in KCyAq to oxidise in air (Eaton a. Fittig, *A.* 145, 157); or by adding manganous acetate to warm KCyAq until the liquid is deep-red, filtering, and cooling (Christensen, *J. pr.* [2] 31, 163). Reddish-brown needles, isomorphous with K_3FeCy_6 (Rammelsberg, *P.* 42, 112; Handl, *W. A. B.* 32, 246). By long boiling with water all Mn is ppd. as hydroxide. Other manganicyanides described are $Ba_3(MnCy_6)_2$, $Ca_3(MnCy_6)_2$, and $Na_3MnCy_6.2H_2O$ (Eaton a. Fittig, *A.* 145, 157). The manganicyanides are reduced to manganocyanides by Na-amalgam (Descamps, *A. Ch.* [5] 24, 178).

Mercury cyanides. Only one cyanide of Hg is known, $HgCy_2$; it forms very many double cyanides, and also combines with many other salts to form double compounds. When Hg_2O is heated with HCNAq, $HgCy_2$ and Hg are formed.

Mercuric cyanide $HgCy_2$. Prepared by boiling Prussian blue with HgO and water; or by boiling 1 part K_4FeCy_6 with 2 parts $HgSO_4$ and 8 parts water; or by dissolving HgO in slight excess of HCNAq and crystallising. White quadratic prisms (De la Provostaye, *A. Ch.* [3] 6, 159; Kopp, *Einleitung in d. Krystallog.* p. 163). S.G. 4·0 (Schröder, *B.* 13, 1070). Very poisonous. Sol. in about 8 parts water at ordinary temperature, much more sol. in hot water, insol. in absolute alcohol. When heated gives Hg, Cy, and paracyanogen (Johnston, *A.* 22, 280; Troost a. Hautefeuille, *C. R.* 66, 735, 795). Solution not ppd. by alkalis; but readily decomposed by H_2S, also by HClAq; very slightly decomposed by other dilute acids in the cold (Plugge, *Fr.* 1879. 408). Decomposed by heating with conc. H_2SO_4; decomposed by Cl, Br, and I, giving $HgCl_2$, &c., and CyCl, &c., action of Cl is attended with explosions (Bonis, *A.* 56, 267; 64, 305; Weith, *B.* 6, 1705; Serullas, *A. Ch.* 35, 293; Stenhouse, *A.* 33, 92). H.F. [Hg,Cy^2] = 18,950; [$HgCy^2$,Aq] = −2,970 (*Th.* 3, 512).

Mercuric oxycyanide $HgCy_2.HgO$. Small needles, formed by dissolving HgO in warm $HgCy_2Aq$, and crystallising. Very slightly sol. in water; explodes when heated (Johnston, *T.* 1839. 113; Schlieper, *A.* 59, 10; Clarke, *B.* 11, 1504). Joannis (*C. R.* 93, 271) gives the thermal data [$HgCy^2$,HgO] = 2,400.

Double cyanides containing mercuric cyanide:—$HgCy_2.2KCy$; obtained as transparent octahedra, unchanged in air, by dissolving $HgCy_2$ in hot KCyAq and crystallising, or by heating $HgCy_2$ with HCyAq and K_2CO_3 (Geuther, *A.* 106, 241). H.F. [Hg,Cy^2,2KCyAq] = 27,780: [$HgCy^2$,2KCyAq] = 8,830; [$HgCy^2$Aq,2KCyAq] = 11,800 (*Th.* 3, 472). Dissolves in c. 4 parts cold water; solution gives pps. with soluble salts of Zn, Pb, &c., these pps. being double cyanides of Hg and the other metal; the following have been isolated:—$3HgCy_2.2CdCy_2$ (Schuler, *A.* 87, 46); $HgCy_2.HgO.7AgCy$ (Bloxam, *B.* 16, 2669); $HgCy_2.N(CH_3)_4Cy$ (Claus a. Merck, *B.* 16, 2737).

Double compounds of mercuric cyanide with metallic salts (Desfosses, *J. Chim. Méd.* 6, 261; Geuther, *A.* 106, 241; Dexter, *C. C.* 1862. 597; Brett, *P. M.* [3] 12, 235; Poggiale, *C. R.* 23, 762; Liebig, *S.* 49, 253; Weeren, *P.* 93, 461; Clarke, *B.* 11, 1504; Ahlén, *Bl.* [2] 27, 365; Caillot, *A. Ch.* [3] 12, 235; 19, 220; Berthemot, *P.* 22, 620; Kletzinsky, *Z.* 1866. 127; Nylander, *J. pr.* 79, 379; Wohler, *P.* 1, 231; Kessler, *P.* 74, 274; Caillot a. Podevin, *J. Ph.* 11, 246; Rammelsberg, *P.* 42, 131; 85, 145; Darby, *A.* 65, 204; Kane, *A.* 35, 356; Bockmann, *A.* 22, 153; Philipp, *P.* 131, 86; Winckler, *Buchner's Repert.* 31, 459; Claus a. Merck, *B.* 16, 2737; Custer, *A.* 68, 323; Apjohn, *P. M.* 9, 401).

I. *With chlorides*: with NH_4Cl, $BaCl_2$, $CaCl_2$, $MgCl_2$, $SrCl_2$, NaCl, $MnCl_2$, $ZnCl_2$ (Brett, Poggiale); with KCl (Defosses, Geuther, Dexter); with $CoCl_2$, $FeCl_3$, $NiCl_2$, $SnCl_4$ (Poggiale, Dexter); with $HgCl_2$ (Poggiale, Liebig, Weeren, Clarke); with chlorides of Ce, Di, Sr, La, and Y (Ahlén).

II. *With bromides*: with $BaBr_2$, $SrBr_2$, NaBr (Caillot); with $CaBr_2$ (Custer); with KBr (Brett, Caillot, Berthemot).

III. *With iodides*: with CaI_2 (Poggiale); with BaI_2, SrI_2, NaI (Custer); with KI (Apjohn, Caillot, Geuther, Kletzinsky).

IV. *With other metallic salts*: with $KClO_3$ (Poggiale); with nitrates of Cd, Co, Cu, Fe, Mn, Ni, Zn (Nylander); with $AgNO_3$ (Wöhler, Geuther); with $HgNO_3$ (Geuther); with $K_2S_2O_3$ (Kessler); with $K_2C_2O_4$ and $Ag_2C_2O_4$ (Caillot a. Podevin, Rammelsberg, Darby); with K_4FeCy_6 (Kane); with sulphocyanides of Ba, Ca, Mg, K (Böckmann, Philipp); with $H.CO_2NH_4$ (Poggiale); with $H.CO_2K$ (Winckler); with $Na.C_2H_3O_2$ (Custer).

V. *With organic ammonium derivatives and alkaloids.* $HgCy_2$ reacts with $N(CH_3)_4I$ to form two isomeric compounds: a white salt $HgCy_2.N(CH_3)_4I$, and a yellow salt $HgCyI.N(CH_3)_4Cy$ (Claus a. Merck). $HgCy_2$ forms double compounds with aniline cyanhydride, with iodo-ethyl quinine, iodo-ethyl cinchonidine, and iodo-ethyl strychnine (Claus a. Merck).

Nickel cyanides. Only one cyanide of Ni is known, $NiCy_2$; it forms several double cyanides; neither nickelo-cyanides nor nickeli-cyanides corresponding to the cobalto- and cobalti-cyanides have been isolated.

Nickelous cyanide $NiCy_2.xH_2O$. Apple-green pp. obtained by adding KCyAq to solution of a Ni salt, or HCNAq to Ni acetate solution. Loses all water at c. 200°; at higher temperatures decomposes, evolving Cy and N, and leaving Ni and a carbide of Ni. Soluble in excess of KCyAq to form $NiCy_2.2KCy$ (Wohler, *Gehlen's Journ.* 6, 234; Rammelsberg, *P.* 42, 114).

Double cyanides containing nickelous cyanide. $NiCy_2.2KCy.H_2O$; obtained by adding excess of KCyAq to solution of a Ni salt, evaporating, and crystallising. Red-yellow monoclinic prisms; S.G. 1·875 at 11°. Loses all water at 100°. Solution decomposes slowly on heating (Balard, *C. R.* 19, 909; Rammelsberg, *P.* 42, 114; 90, 35; Clarke, *J.* 1877. 43). The following double cyanides have also been isolated: $NiCy_2.2NH_4Cy$ (Wöhler, *Gehlen's Journ.* 6, 234); $NiCy_2.BaCy_2.3H_2O$ (Wöhler, *l.c.*; Weselsky, *B.* 2, 588; Mouthiers, *A.* 64, 297); $NiCy_2.CaCy_2.xH_2O$ (Wöhler, *l.c.*); $NiCy_2.2NaCy.3H_2O$ (Wöhler, *l.c.*; Rammelsberg, *P.* 42, 114); $NiCy_2.SrCy_2.xH_2O$ (Handl, *W. A. B.* 32, 246). Solutions of these double cyanides are decomposed by dilute acids with ppn. of $NiCy_2$, and evolution of HCy; HgO decomposes them ppg. $NiCy_2$ and NiO; Cl or Br ppts. Ni_2O_3.

Niobium cyanide. No cyanide of Nb has been isolated. When Nb_2O_5 is strongly heated with Na_2CO_3 and charcoal in a current of air, a metal-like solid is formed resembling the compound of Ti with Cy and N; this solid is possibly analogous in composition to the Ti compound (*v.* TITANIUM CYANIDES) (Joly, *C. R.* 82, 1195).

Osmium cyanides. One cyanide of Os, $OsCy_2$, and *osmocyanhydric acid* H_4OsCy_6 and some of its salts, have been prepared.

Osmous cyanide $OsCy_2$. Dark violet solid obtained by continued boiling H_4OsCy_6 with HClAq (Martius, *A.* 117, 357).

Osmocyanhydric acid H_4OsCy_6. Obtained by adding conc. HClAq to K_4OsCy_6Aq (*q.v.*), collecting the pp. which forms, washing it with conc. HClAq, and crystallising from alcohol by adding a few drops of ether. White hexagonal prisms; unchanged in dry air; in moist air decomposes to $OsCy_2$ and HCN; sol. in water and alcohol, ppd. by a little ether (Martius, *A.* 117, 357).

Osmocyanides. $K_4OsCy_6.3H_2O$; prepared by dissolving 1 part osmic acid in KOHAq until the liquid remains feebly alkaline, adding 1¼ parts KCy, evaporating to dryness, heating in a closed vessel, dissolving in water, and crystallising once or twice (Martius, *A.* 117, 357; Claus, *Beiträge z. Chemie d. Platinmetalle* [Dorpat, 1854], or *J.* 1855. 444; Claus, *J. pr.* 85, 129). Yellow-white plates isomorphous with K_4FeCy_6 (Claus, *J. pr.* 85, 129). The following osmocyanides have also been described: $Ba_2OsCy_6.6H_2O$ (Martius, *A.* 117, 357); $BaK_2OsCy_6.3H_2O$ (Martius, *l.c.*). K_4OsCy_6Aq gives pps. with many metallic salts.

Palladium cyanides. Two cyanides of Pd, $PdCy_2$ and $PdCy_4$, are known. Several double cyanides of $PdCy_2$ have been prepared. They may be regarded as derivatives of the hypothetical palladium-cyanhydric acid H_2PdCy_4; this acid has not been isolated, but the analogies in crystalline form and general properties between the double cyanides of $PdCy_2$ and those of $PtCy_2$ point to the Pd salts as being derived from H_2PdCy_4; the acid H_2PtCy_4 is known.

Palladous cyanide $PdCy_2$. Yellow-white pp. obtained by adding $HgCy_2Aq$ to neutral $PdCl_2$ solution. Decomposed by heat to Pd and Cy; not decomposed by ordinary acids nor by HgO; soluble in NH_3Aq, from which solution the compound $PdCy_2.2NH_3$ separates in white needles; soluble in KCyAq forming $PdCy_2.2KCy$ (Berzelius, *P.* 13, 460; Fehling, *A.* 39, 119; Rossler, *Z.* 1866. 175). Joannis (*C. R.* 95, 295) gives some thermal data: $[Pd,Cy^2] = 23,600$ (solid $PdCy_2$ from gaseous Cy and solid Pd); $[PdO,2HCyAq] = 44,800$ (giving solid $PdCy_2$).

Palladic cyanide $PdCy_4$. Reddish pp. easily decomposing with evolution of HCN; obtained by shaking $HgCy_2Aq$ with $PdCl_4.2KCl$.

Double cyanides of palladous cyanide, or pallado-cyanides. $PdCy_2.2NH_4Cy$ (or $(NH_4)_2PdCy_4$); obtained by adding $HgCy_2Aq$ to an ammoniacal solution of a palladous salt; said to be ppd. by adding HCNAq to $PdCl_2.2NH_4Cl$ (Croft, *J. pr.* 104, 64; *v.* also Rössler, *Z.* 1866. 175). $PdCy_2.BaCy_2$(or$BaPdCy_4$)$.4H_2O$; large greenish monoclinic prisms; formed by adding HCNAq to a mixture of $PdCy_2$ and $BaCO_3$ (Rössler, *Z.* 1866. 175; Weselsky, *B.* 2, 588). $PdCy_2.2KCy$ (or K_2PdCy_4); obtained by dissolving $PdCy_2$ or Pd black in KCyAq, and crystallising. Crystallises with $3H_2O$ in white monoclinic crystals, or with H_2O in lustrous tablets (Rössler, *Z.* 1866. 175). The following double cyanides are also described by Rössler (*l.c.*); $PdCy_2.CaCy_2.4H_2O$; $PdCy_2.CuCy_2$; $PdCy_2.PbCy_2$; $PdCy_2.MgCy_2.4H_2O$, this compound forms the complex cyanide $MgPdCy_4.MgPtCy_4.14H_2O$ (Rossler); $PdCy_2.HgCy_2$; $PdCy_2.2AgCy$; $PdCy_2.2NaCy$. Most of these double cyanides are isomorphous with the corresponding platinocyanides which are derivatives of the acid H_2PtCy_4. Solutions of the Pd double cyanides are decomposed, slowly in air, more quickly by acids, with separation of $PdCy_2$; H_2S ppts. PdS; Zn ppts. Pd.

Platinum cyanides. Platinum cyanide $PtCy_2$ is known; also platincyanhydric acid H_2PtCy_4, and many salts derived therefrom; there are also several compounds which may be regarded as additive compounds of the platinocyanides with halogens, or better as derivatives of *perchloro-* (*bromo-* or *iodo-*) *platincyanhydric acid*

$H_2X_2PtCy_4$; and finally there are some compounds of doubtful composition.

Platinous cyanide $PtCy_2$. Obtained by heating $PtCy_2.2KCy$ (prepared by heating KCyAq with conc. $PtCl_2Aq$, or by warming $PtCl_4.2NH_4Cl$ with KCy and a little KOH) with $HgCl_2$; or by heating $PtCy_2.HgCy_2$ (prepared by adding $HgCl_2Aq$ to $PtCy_2.2KCyAq$) (Dobereiner, *A.* 17, 250; Quadrat, *A.* 63, 164). Also formed by heating $PtCy_2.2NH_4Cy$ to 300° (Schafarik, *J. pr.* 66, 385); also by heating $PtCy_2.2KCy$ with conc. H_2SO_4 (Knop a. Schnedermann, *J. pr.* 37, 461); also by ppg. neutral $PtCl_2Aq$ by $HgCy_2Aq$ (Rössler, *Z.* 1866. 175); also, along with other products, by heating H_2PtCy_6 with HNO_3Aq (Schafarik, *l.c.*). Sulphur-coloured solid; insol. in water, acids, and alkalis; when heated gives Cy and Pt; dissolves in alkali cyanides forming platinocyanides; when freshly ppd. dissolves in NH_3Aq.

Platinocyanhydric acid H_2PtCy_4. HCN is passed into a mixture of 1 part $PtCl_2$ with 1½ parts $BaCO_3$ suspended in 5 parts water kept nearly boiling; the passage of HCN is continued so long as CO_2 is evolved; $BaPtCy_4.4H_2O$ crystallises out on cooling; this salt is dissolved in water (1 part dissolves in 33 parts water at 16°), and an equivalent quantity of H_2SO_4Aq is added; the filtrate from the ppd. $BaSO_4$ is evaporated at a gentle heat and crystallised (Weselsky, *J. pr.* 69, 276). Or $CuPtCy_4$ is prepared by adding $PtCy_2.2KCyAq$ to $Cu(NO_3)_2Aq$, and the Cu salt is decomposed by H_2S (Quadrat, *A.* 63, 164). Crystallises with $5H_2O$ in cinnabar-red prisms with blue sheen on surface, or with more than $5H_2O$ in yellow-green, metal-like crystals, or in blue-black needles. Deliquescent. Very sol. in water and alcohol. Heated, decomposes above 140° to HCN and $PtCy_2$. Carbonates are decomposed by H_2PtCy_4.

Platinocyanides. These salts generally form very beautiful dichroic crystals; the soluble salts may be prepared by decomposing $BaPtCy_4$ by the various metallic sulphates; the insoluble platinocyanides may be formed by adding the various metallic salts to K_2PtCy_4Aq.

Ammonium platinocyanide $(NH_4)_2PtCy_4.H_2O$. White, translucent needles; crystallises with $2H_2O$ as yellow prisms; both with blue reflection. V. sol. water (Schafarik, *J. pr.* 66, 385; Quadrat, *A.* 63, 164; Knop a. Schnedermann, *J. pr.* 37, 461). An hydroxylammonium salt $(NH_4O)_2PtCy_4.2H_2O$ is known; and also the double salt $(NH_4.NH_4O)PtCy_4.3\frac{1}{2}H_2O$ (Scholz, *M.* 1, 900).

Barium platinocyanide $BaPtCy_4.4H_2O$. Prepared by passing HCN into 5 parts almost boiling water holding 1 part $PtCl_2$ and 1½ parts $BaCO_3$ in suspension, until CO_2 ceases to be evolved, and crystallising (Weselsky, *J. pr.* 69, 276); $PtCl_4$ may be used in place of $PtCl_2$, in which case O is evolved ($PtCl_4 + 3BaCO_3 + 4HCN = BaPtCy_4 + 2BaCl_2 + 2H_2O + 3CO_2 + O$; Weselsky, *J. pr.* 103, 566). Monoclinic prisms. S.G. 3·054 (Schabus, *W. A. B.* 1850. 582). Crystals appear green in direction of principal axis, and sulphur yellow with blue-violet sheen in direction at right angles to this. Soluble in 33 parts water at 16°, considerably more sol. at 100°. Loses all water at 180°, and begins to decompose. Forms double compounds, $BaPtCy_4.K_2PtCy_4$ (Martius, *A.* 117, 357), and $BaPtCy_4.Rb_2PtCy_4$ (Ditscheiner, *W. A. B.* 50, 373).

Magnesium platinocyanide $MgPtCy_4.7H_2O$. Prepared by adding $MgSO_4Aq$ to $BaPtCy_4Aq$, filtering, evaporating to dryness, dissolving in a boiling mixture of alcohol and ether, and crystallising. Red quadratic prisms, showing greenish on the surfaces near the middle of the crystals and blue near the extremities (Haidinger, *P.* 77, 89; Werther, *J. pr.* 76, 186; Greiss, *P.* 106, 645). At 40° loses water, turning yellow. The yellow salt may be obtained in fine crystals by evaporating an alcoholic solution of the salts with $7H_2O$ over H_2SO_4; the crystals contain $5H_2O$ (Werther, *J. pr.* 76, 186). Becomes colourless at c. 100°; at 150° still contains $2H_2O$; dehydrated at 200°-230°, becoming orange yellow (Werther, *l.c.*). (For more details *v.* Schafarik, *J. pr.* 66, 385; Quadrat, *A.* 63, 164; 70, 300; Weselsky, *J. pr.* 69, 276.)

Mercuric platinocyanide $HgPtCy_4$. White pp. obtained by adding $HgCl_2Aq$ to K_2PtCy_4Aq (Schafarik, *J. pr.* 66, 385).

Platino-ammonium platinocyanide $PtPtCy_4.4NH_3$. (*Platino-cyano-diplatoso-ammonium. Ammonium-platinammonium platinocyanide.*) White pp. obtained by adding KCyAq to ammoniacal $PtCl_2$ solution. With $AgNO_3Aq$ forms Ag_2PtCy_4 and $Pt(NO_3)_2.4NH_3$ (Knop a. Schnedermann, *J. pr.* 37, 461; Buckton, *A.* 78, 328).

Potassium platinocyanide $K_2PtCy_4.3H_2O$. Clear yellow rhombic prisms, with blue appearance in direction of principal axis. S.G. 2·4548 at 16° (Clarke, *J.* 1877. 43). Effloresces in air, becoming nearly white with slight orange tint. Does not decompose at c. 600°. Sl. sol. cold, v. sol. hot, water. Decomposed by H_2SO_4Aq in the cold, giving $PtCy_2$ and CO_2. Solution gives white pp. with mercurous salts with Hg not in excess, and a blue pp. with excess of Hg salts; this reaction characterises platinocyanides. The salt may be obtained by dissolving $PtCl_4.2NH_4Cl$ with a little KOH in a conc. boiling solution of KCy, and crystallising from water (Martius, *A.* 117, 357). It is also produced by boiling Pt black with conc. KCyAq (Deville a. Debray, *C. R.* 82, 241); also by heating a mixture of Pt black and K_4FeCy_6 nearly to redness, treating with water, filtering, evaporating, and recrystallising from water the crystals which separate.

Silver platinocyanide Ag_2PtCy_4. White pp. by adding $AgNO_3Aq$ to K_2PtCy_4Aq. Combines with NH_3 to form $Ag_2PtCy_4.2NH_3$ (Knop a. Schnedermann, *J. pr.* 37, 461); prepared by adding K_2PtCy_4Aq to ammoniacal $AgNO_3Aq$, or to a solution of $AgCO_3$ in $(NH_4)_2CO_3Aq$. Sol. dilute NH_3Aq, not in water.

Besides the preceding platinocyanides, the following have been isolated:—$CaPtCy_4.5H_2O$; and $CaPtCy_4.K_2PtCy_4$ (Dobereiner, *A.* 17, 250; Martius, *A.* 117, 357; Quadrat, *A.* 70, 300). $CdPtCy_4$; $CdPtCy_4.2NH_3.H_2O$; and $PbPtCy_4.xH_2O$ (Martius, *l.c.*). $CuPtCy_4.xH_2O$; $CuPtCy_4.2NH_3.H_2O$; $Na_2PtCy_4.3H_2O$; $NaK.PtCy_4.3H_2O$; $SrPtCy_4.5H_2O$ (Schafarik, *J. pr.* 66, 385; Quadrat, *A.* 63, 164; Martius, *l.c.*). $Ce_2(PtCy_4)_3.18H_2O$; $La_2(PtCy_4)_3.18H_2O$ (Czudnowicz, *J. pr.* 80, 16). $CoPtCy_4.2NH_3$; $NiPtCy_4.2NH_3.H_2O$; $ZnPtCy_4.2NH_3.H_2O$ (Knop

a. Schnedermann, *J. pr.* 37, 461).
$Di_2(PtCy_4)_3.18H_2O$ (Clève, *Bl.* [2] 21, 246).
$Er_2(PtCy_4)_3.21H_2O$; $Y_2(PtCy_4)_3.21H_2O$ (Clève a. Hoeglund, *Bl.* [2] 18, 197). $Li_2PtCy_4.xH_2O$; $Li(NH_4O)PtCy_4.3H_2O$ (Scholz, *M.* 1, 900).
$Rb_2PtCy_4.xH_2O$ (Ditscheiner, *W. A. B.* 50, 373).
Tl_2PtCy_4; $Tl_2PtCy_4.Tl_2CO_3$ (Friswell, *A.* 159, 383; F. a. Greenaway, *B.* 10, 1858). $Th(PtCy_4)_2.16H_2O$ (Clève, *Bl.* [2] 21, 116).

The salts $(NH_3Me)_2PtCy_4$, $(NH_3Et)_2PtCy_4$, $(NH_2Et_2)_2PtCy_4$, and $(NHEt_3)_2PtCy_4$, have been isolated (Debus, *A.* 128, 200; Scholz, *M.* 1, 900). Et_2PtCy_4 is described by Than (*A.* 107, 315); also salts of aniline, paratoluidine, and α-naphthylamine (Scholz, *l.c.*). Salts of alkaloids are also known (*v.* Schwarzenbach, *Vierteljahr. Pharm.* 6, 422; Delfs, *Fr.* 3, 152).

Halogen addition products of platinocyanides, or salts of perchloro-, perbromo-, and periodo-platinocyanhydric acid. These salts have the general form

$$M_2PtCy_4.X_2 \text{ where } M = K, Na, \frac{Ba}{2}, \frac{Pb}{2}, \frac{Ni}{2}, \frac{Al}{3}, \&c.,$$

and X = Cl, Br, or I. They were first obtained by Hadow (*C. J.* 13, 106), and have been examined also by Blomstrand (*J. pr.* [2] 3, 207), and by Holst (*Bl.* [2] 22, 347). Alkalis, or $AgNO_3Aq$, withdraw halogen from these salts re-producing the platinocyanides. These salts give white pps with excess of $HgNO_3Aq$, whereas platinocyanides give blue pps. under same conditions. When conc. solutions of the perhaloid-platinocyanides are mixed with conc. solutions of platinocyanides, double compounds of the form $5M_2PtCy_4.M_2PtCy_4X_2$ are ppd. (*v.* CHLORO- &c. PLATINOCYANIDES, *infra*). These salts bleach in presence of alkalis; the chloro- and bromo- salts decompose KI.

Potassium perchloroplatinocyanide $K_2PtCy_4.Cl_2.2H_2O$ (Knop a. Schnedermann, *J. pr.* 37, 461). This salt was formerly regarded as $PtCy_4.2KCl$, *i.e.* as a double compound of KCl with the hypothetical $PtCy_4$; but the researches of Hadow show that it is rather to be looked on as the final product of the reaction of Cl with K_2PtCy_4, the intermediate product being the salt (described below) $5K_2PtCy_4.K_2PtCy_4.Cl_2$, which is called by Hadow *potassium-chloroplatinocyanide.* Potassium perchloroplatinocyanide is prepared by dissolving K-chloroplatinocyanide (*q. v.*) in nearly boiling *aqua regia* and crystallising (K. a. S.), or by oxidising the same salt by $KMnO_4$ in presence of HCl, evaporating at 100°, and crystallising. Large rhomboidal triclinic plates; v. sol. water and alcohol; very efflorescent; heated gives off Cy, leaving KCl and K_2PtCy_4, and at a higher temperature gives KCl and Pt. Partially reduced by Zn and NH_3Aq, or by SO_2Aq, to mixture of K_2PtCy_4 and $6K_2PtCy_4.Cl_2$ (K-chloroplatinocyanide). When conc. solution of $K_2PtCy_4.Cl_2$ and K_2PtCy_4 are mixed crystals of the chloroplatinocyanide ($5K_2PtCy_4.K_2PtCy_4.Cl_2$) are deposited.

The following **perchloroplatinocyanides** have been isolated, besides the K salt:— $(NH_4)_2X.2H_2O$; $BaX.5H_2O$; CaX; $MgX.xH_2O$; $MnX.2H_2O$ (Holst, *Bl.* [2] 22, 347) [X = $PtCy_4.Cl_2$].

Perchloro-platinocyanhydric acid $H_2PtCy_4.Cl_2.4H_2O$ (Holst, *l.c.*). Obtained by decomposing the Ba salt (itself produced by passing Cl into $BaPtCy_4Aq$) by H_2SO_4Aq, filtering and crystallising. White crystals; very soluble in water and alcohol.

Perbromo-platinocyanhydric acid $H_2PtCy_4.Br_2.xH_2O$ (Holst, *l.c.*) is obtained by adding Br to $BaPtCy_4Aq$ and crystallising; it forms white crystals very sol. in alcohol and ether.

Several **perbromo-platinocyanides** and some **periodoplatinocyanides** have been isolated; they are produced by the action of Br or I on the platinocyanides; the salts of the alkalis and alkaline earths are very soluble in water and may generally be easily crystallised; most of the salts of the heavy metals are insol. or only sl. sol. in water. Holst (*l.c.*) describes the following:—[X = $PtCy_4.Br_2$] $Al_2.3X.22H_2O$; $(NH_4)_2X$; $BaX.5H_2O$; BeX; $CdX.xH_2O$; $CoX.5H_2O$; $PbX.2H_2O$; Li_2X; $MgX.xH_2O$; $NiX.xH_2O$; K_2X; Na_2X; $SrX.7H_2O$; $ZnX.5H_2O$. The periodo- salts described by Holst are $BaPtCy_4.I_2.xH_2O$, and $K_2PtCy_4.I_2$.

Double compounds of platinocyanides with perhaloid platinocyanides; or chloro- &c. platinocyanides, or chloro- &c. platinidplatinocyanides. These salts were formerly supposed to be double compounds of KCl &c. with the hypothetical $PtCy_3$, of the form $M_2PtCy_5 = PtCy_3.2MCy$. They are produced by the reaction of Cl, Br, HNO_3, and other oxidisers, with the platinocyanides M_2PtCy_4. The change was supposed to be somewhat analogous to that which occurs when a ferrocyanide (M_4FeCy_6) is oxidised to a ferricyanide (M_3FeCy_6); thus $2K_4FeCy_6 + O = 2K_3FeCy_6 + K_2O$, and $3K_2PtCy_4 + O = 2K_2PtCy_5 + PtCy_2 + K_2O$. In accordance with this conception, the compounds were called *platinicyanides* (and sometimes *platinosesquicyanides* when their composition was indicated by the formula $Pt_2Cy_6.4MCy$). Hadow (*C. J.* 13, 106), however, showed that the salt of this series obtained by the limited action of Cl on K_2PtCy_4 contained Cl; his analyses and methods of synthesis of the salt led him to give it the formula $(K_2PtCy_4)_6Cl_2$, and to indicate its formation by the reaction $6K_2PtCy_4 + Cl_2 = 6(K_2PtCy_4)Cl_2$. The synthesis of the same salt by mixing conc. solution of K perchloroplatinocyanide ($K_2PtCy_4.Cl_2$) and K platinocyanide (K_2PtCy_4) shows that the formula $6(K_2PtCy_4)Cl_2$ is better written so as to indicate that the salt is a double compound, viz. $5K_2PtCy_4.K_2PtCy_4.Cl_2$; this formula is confirmed by the fact that reducing agents (*e.g.* SO_2Aq, or Zn and NH_3Aq) decompose the salt to a mixture of $K_2PtCy_4.Cl_2$ and K_2PtCy_4; moreover, the salt in question reacts with excess of Cl to form $K_2PtCy_4.Cl_2$, and with excess of I or Br to form $K_2PtCy_4.I_2$ or $K_2PtCy_4.Br_2$, respectively. Holst (*B.* 8, 124) got results which show that although the composition of the chloro- &c. platinocyanides is always to be represented by the formula $xM_2PtCy_4.yM_2PtCy_4.X_2$ yet the ratio of $x:y$ is not always 5:1.

Potassium chloroplatinocyanide, or *Potassium chloroplatinidplatinocyanide,* $5K_2PtCy_4.K_2PtCy_4.Cl_2.21H_2O$ (Hadow, *C. J.* 13, 106; Knop, *A.* 43, 111). Cl is passed into warm K_2PtCy_4Aq so conc. that crystals are deposited on cooling; the crystals are dried between paper and recrystallised from water acidulated with HCl (Knop). Hadow divides a solution of K_2PtCy_4 into 6 parts; into $\frac{1}{6}$ he passes Cl until the liquid is saturated ($K_2PtCy_4.Cl_2$ is thus formed), he then adds the remaining $\frac{5}{6}$ and evaporates. Green prismatic crystals, with red metal-like surface colour by reflected light. Sol. in water giving colourless solution, insol. in alcohol. Gives off part of H_2O over H_2SO_4, becoming black; loses $18H_2O$ at 100° and the rest at c. 180°; when strongly heated gives off Cy.

Holst (*B.* 8, 124) obtained the salt $10SrPtCy_4.SrPtCy_4.I_2.xH_2O$.

Weselsky (*J. pr.* 69, 276) describes some salts obtained by the action of HNO_3Aq on platinocyanides; he regards these as platinocyanides or platinum sesquicyanides ($Pt_2Cy_6.4MCy$); but it is very probable that they are analogous to Hadow's double compounds of platinocyanides with perchloro- &c. platinocyanides, only that the halogen is replaced either by NO_2 or NO_3 (*cf.* Hadow, *C. J.* 13, 106; also *v.* Martius, *A.* 117, 357, for reaction of $PbPtCy_4$ with HNO_3 whereby $xPbPtCy_4.yPbPtCy_4(NO_2)$ seems to be produced).

The compound obtained by Hadow by the action of PbO_2 on K_2PtCy_4 in H_2SO_4 solution seems also to belong to this class and to have the halogen atoms replaced by the radicle SO_4.

Potassium cyanide KCy. S.G. $\underline{16^\circ}$ 1·52 (Bödeker). [K, CN] = 65,350; [K, N, C] = 32,500; [KCy, Aq] = −3,010 (*Th.* 3, 235); [KOHAq, HCNAq] = 2,770 (*Th.* 1, 160).

Occurrence.—In blast furnaces.

Formation.—1. By fusing K in Cy or in HCN gas.—2. By fusing K_2CO_3 with nitrogenous carbon.—3. By passing N over a strongly heated mixture of C and KOH or K_2CO_3.—4. By deflagrating KNO_3 with K acetate, tartrate, &c., especially by heating a mixture of KNO_2, K_2CO_3, and $KC_2H_3O_2$ (Desfosses, *A. Ch.* 38, 158; Fownes, *J. pr.* 26, 412; Delbrück, *A.* 64, 296; Bunsen a. Playfair, *J. pr.* 42, 397; Reiken, *A.* 79, 77; Langlois, *A. Ch.* [3] 52, 326; Roussin, *C. R.* 47, 875).—5. By passing NH_3 over a heated mixture of C and K_2CO_3 or KOH (Kuhlmann, *A.* 38, 62).

Preparation.—1. Ordinary commercial KCN (containing KCNO) is prepared by fusing dry K_4FeCy_6 with K_2CO_3[$2K_4FeCy_6 + 2K_2CO_3 = 10KCN + 2KCNO + 2Fe + 2CO_2$]; the fused mass is poured off from the iron.—2. HCN gas is passed into alcoholic solution of KOH (1 part KOH in 3 parts alcohol) (Wiggers, *A.* 29, 65). An aqueous solution of pure KCN is obtained by passing HCN into KOHAq.—3. Nearly pure KCN is prepared by fusing dry K_4FeCy_6 in absence of air, and treating with 50 p.c. hot alcohol (Geiger, *A.* 1, 46); [$2K_4FeCy_6 = 8KCN + 2FeC_2 + 2N_2$].

Properties.—Crystallises from alcohol, or by slowly cooling the fused salts, in white cubes, or octahedra, v. sol. in water; deliquescent; sl. sol. in strong alcohol. *Very poisonous.* Melts easily, and volatilises unchanged (in absence of moisture) at full red heat.

Reactions.—1. *Aqueous solution* decomposes in air, slowly at ordinary temperature, rapidly at 100°, giving HCO_2K and NH_3.—2. *Melted in air* forms KCNO.—3. Heated with *metallic oxides* gives KCNO and metal; thus acts as an energetic reducer, *e.g.* reduces oxides of Pb, Fe, Sb, Sn, &c., &c., when heated with them.—4. Heated with *potassium chlorate* or *nitrate*, detonates violently.—5. Reduces *alkaline sulphates* to sulphides by heating with them.—6. With *solution of potassium permanganate*, KCN forms CO_2, HNO_3, HNO_2, $H_2C_2O_4$, H_2CO_3, and $CO2NH_2$ (Schlagdenhauffen, *J.* 1863. 305). 7. With *alkali polysulphides*, KCNAq forms KCNSAq.—8. With *iodine* in conc. solution KCN forms KI and CyI.—9. With *sodium thiosulphate* forms NaCNS.—10. With *potash* produces NH_3 and HCO_2K; heated to redness with KOH, K_2CO_3 is formed and H evolved.

Combination.—1. KCNAq dissolves many *metallic cyanides* forming double cyanides, *e.g.* $HgCy_2$, AuCy, $PtCy_2$, Cu_2Cy_2, &c. (*v. various metallic cyanides*).—2. When *sulphur dioxide* is passed into cold conc. KCNAq, two compounds are formed, $CNK.SO_2.H_2O$ and $CNK.SO_3KH.SO_2$; they may be crystallised (Etard, *C. R.* 88, 649).

Testing KCN *for common impurities.*—The chief impurities in ordinary KCN are KCNO, K_2CO_3, K_2S, KNCS, $KHCO_2$, K_4FeCy_6, K_2SO_4, and KCl. K_2CO_3 is detected by treating with alcohol at 80° and examining the insoluble portion by the ordinary tests. K_2S; Pb salts give a black pp., in absence of K_2S a white pp. is formed. KCNS; HClAq is added and the HCN is removed by warming; a few drops of $FeCl_3Aq$ are added, when a deep-red colour shows KNOS. KCNO; alcohol at 80° is added and the solution is acidulated, effervescence shows KCNO. $KHCO_2$; a current of CO_2 is passed through until HCN is removed, the liquid is evaporated to dryness, the residue is distilled with H_2SO_4Aq, and to the distillate are applied the ordinary tests for formic acid. K_4FeCy_6; pure $FeCl_3Aq$ gives blue pp. or blue colouration. K_2SO_4; HCN is removed by warming with HClAq, and $Ba2NO_3Aq$ is added. KCl; the specimen is heated with 2 parts KNO_3 and 10 parts Na_2CO_3, the fused mass is heated with water, and $AgNO_3$ and HNO_3Aq added to the aqueous solution to pp. AgCl.

Rhodium cyanides. Rh_2Cy_6, and a rhodicyanide K_3RhCy_6, are known.

Rhodium sesquicyanide Rh_2Cy_6. Carmine-red powder, obtained by adding hot conc. acetic acid to K_3RhCy_6 (Martius, *A.* 117, 357). Dissolves in KCNAq with re-formation of K_3RhCy_6.

Potassium rhodicyanide K_3RhCy_6. Monoclinic crystals: easily decomposed by acids; formed by fusing $RhCl_4.2NH_4Cl$ with KCN (Claus, *J.* 1855. 444).

Ruthenium cyanides. No simple cyanide has been isolated; H_4RuCy_6 and some of its salts are known.

Rutheno-cyanhydric acid H_4RuCy_6 (Claus, *J.* 1855. 444). Obtained by adding HClAq and ether to the K salt (*q. v.*); lustrous, iridescent tablets; e. sol. alcohol and water; heated with HClAq, HCN is evolved.

Potassium rutheno-cyanide $K_4RuCy_6.3H_2O$ (Claus, *l.c.*). Obtained by heating KCN with $RuCl_4.2NH_4Cl$; small, white, quadratic tablets, isomorphous with K_4FeCy_6. The solution of this salt gives coloured pps. with salts of Cu, Fe, Pb, and Zn.

Silver cyanide AgCy. Only one cyanide of Ag is known; it forms various double salts.

White, curdy pp. obtained by adding HCNAq or KCNAq to solution of a salt of Ag; excess of KCN must be avoided, as AgCy is sol. KCyAq; the pp. is dried at a temperature under 126°. S.G. c. 3·95 (Schröder, *B.* 13, 1074). H.F. [Ag, Cy] -1,395; [Ag, C, N] = -31,455; [2HCyAg, Ag^2O] = 42,310 (ppd. Ag_2O; formation of solid AgCy) (*Th.* 3, 382). Not blackened by exposure to light. Sol. NH_3Aq; sl. sol. boiling HNO_3Aq; sol. KCNAq.

Reactions.—1. *Heated*, is decomposed to Ag and Cy.—2. *Water* at 280° forms $NH_4.Ag.CO_3$ (Reynoso, *A. Ch.* [3] 45, 111).—3. *Chlorine* forms AgCl and CyCl.—4. *Sulphur* heated with AgCy forms AgNCS. — 5. *Ammonia* dissolves AgCN, forming $AgCN.NH_3$.—6. *Potassium cyanide* dissolves AgCy, forming AgCy.KCy.—7. Decomposed by *sulphuric acid* or *hydrochloric acid*, with evolution of HCN.—8. Decomposed by *sulphuretted hydrogen*, also by *sulphur chloride* (Schneider, *J. pr.* 104, 83).

Combinations.—1. With *ammonia* to form $AgCy.NH_3$; monoclinic tablets, which give off NH_3 in the air; obtained by heating AgCy in NH_3 (Weith, *Z.* 1869. 380; Liebig a. Redtenbacher, *A.* 38, 129).—2. With *silver nitrate* to form $AgCy.AgNO_3$ (or ? $2AgCy.AgNO_3$) (Bloxam, *C. N* 48, 154; Wöhler, *P.* 1, 231); obtained by dissolving AgCy in hot conc. $AgNO_3Aq$.

Double cyanides containing silver cyanide. The alkali salts are obtained by dissolving AgCy in solution of the alkali cyanide and evaporating; the salts of the heavy metals are generally obtained by adding AgCy.KCyAq to solutions of these metals.

Silver-potassium cyanide AgCy.KCy. Regular octahedra; sol. 4 parts water at 20°, and in 25 parts alcohol (85 p.c.). Decomposed by acids with separation of AgCy. H_2S ppts. Ag_2S, except from solutions in much KCNAq (Glassford a. Napier, *P. M.* 15, 66; Rammelsberg, *P.* 38, 376; Baup, *A. Ch.* [3] 53, 462; Béchamp, *J. pr.* 60, 64). H.F. [Ag^2Cy^2,2KCyAq] = 12,980; [Ag^2,Cy^2,2KCyAq] = 15,780 (*Th.* 3, 470). The other important silver double cyanides are:—AgCy.NaCy; 3AgCy.2KCy.NaCy (Baup, *l.c.*); AgCy.TlCy (Fronmüller, *B.* 11, 91); $AgCy.NMe_4Cy$ (Thompson, *B.* 16, 2338; Claus a. Merck, *B.* 16, 2737); $2AgCy.HgCy_2.HgSO_4.H_2O$ (Geuther, *A.* 106, 241).

Sodium cyanide NaCy. Prepared by passing HCN gas into an alcoholic solution of NaOH until NaCy pps. Obtained also by methods similar to those whereby KCy is formed (*v.* POTASSIUM CYANIDE, p. 346). NaCy crystallises with difficulty. According to Joannis (*A. Ch.* [5] 27, 482) two hydrates are obtained by crystallising from alcohol at different temperatures; $2NaCy.H_2O$, and $NaCy.2H_2O$. Joannis (*l.c.*) gives some thermal data:—[Na, Cy] = 60,400 (solid NaCy formed); [NaCy, Aq] = -500; [HCyAq, NaOHAq] = 2,900.

Strontium cyanide $SrCy_2$. Prepared, similarly to $BaCy_2$, by heating $SrFeCy_6$; or preferably by passing HCN vapour into crystals of SrO_2H_2. Unstable salt. Crystallises from solution with $4H_2O$; the crystals are v. deliquescent and absorb CO_2 from the air (Joannis, *A. Ch.* [5] 27, 482; Schulz, *J. pr.* 68, 257). Joannis (*l.c.*) gives the thermal data:—[SrOAq, 2HCyAq] = 6,260.

Thallium cyanides. Two cyanides of Tl are known, TlCy and $TlCy.TlCy_3$.

Thallous cyanide TlCy. Obtained by adding excess of conc. HCNAq to a conc. solution of a thallous salt, and then adding much alcohol and ether. Heavy white pp., e. sol. water, crystallising in lustrous tablets from the hot solution. Decomposed by heating (Fronmuller, *B.* 6, 1178).

Thallo-thallic cyanide $TlCy.TlCy_3$ (= Tl_2Cy_4). Formed by evaporating *in vacuo* a solution of Tl_2O_3 in HCNAq. Large, white, rhombic plates; e. sol. water; decomposed at 125°-130° with rapid evolution of Cy (Fronmuller, *B.* 11, 91).

Double cyanides containing thallous cyanide.—TlCyAq dissolves the cyanides of Hg, Ag, and Zn; when the solutions are crystallised the following salts are obtained:—$2TlCy.HgCy_2$; TlCy.AgCy; $2TlCy.ZnCy_2$ (Fronmüller, *B.* 11, 91). No double cyanides of Tl_2Cy_4 are known.

Titanium cyanides. No cyanide of Ti is known, but the compound Ti_5CN_4 exists; this body is almost certainly a double compound of Ti cyanide with Ti nitride $TiCy_2.3Ti_3N_2$.

Titanium cyano-nitride $TiCy_2.3Ti_3N_2$. This compound is formed in smelting titaniferous iron-stones in the blast furnace (Wöhler, *A.* 73, 34; 74, 212). It may be obtained by very strongly heating K_4FeCy_6 with TiO_2 (Wohler, *l.c.*), by heating KCN in vapour of $TiCl_4$, and by passing N over a mixture of C and TiO_2 heated to the M.P. of Pt (Wöhler a. Deville, *A.* 103, 230). Metal-like, reddish octahedra, resembling metallic Cu. S.G. 5·28. Volatile at very high temperature. Not acted on by boiling HNO_3Aq or H_2SO_4. Sol. HNO_3Aq containing HF. Heated in water-gas is decomposed thus: $Ti_5CN_4 + 10H_2O = CNH + 5TiO_2 + 3NH_3 + 5H_2$. Decomposed when heated with Cl, giving $TiCl_2$, and probably a compound of $TiCl_2$ with CyCl. Heated with KOHAq forms K titanate and NH_3. CuO, PbO, and HgO are reduced to metals when heated with Ti_5CN_4.

Uranium cyanide. None has been certainly isolated. The oxides of U do not dissolve in HCNAq; addition of KCNAq to solution of U chloride ppts. an oxide of U (Rammelsberg, *P.* 59, 2). According to Wittstein (*R. P.* 63, 214), when KCNAq is added to a uranic salt solution a yellow pp. is obtained, sol. in excess of KCNAq, not ppd. again by acids.

Vanadium cyanide. None has been isolated. Berzelius made some observations on the reactions between vanadic acid and HCN (*P.* 22, 26).

Yttrium cyanide. No cyanide has been certainly isolated. Hydrated Y_2O_3 is said to dissolve in HCNAq, and white nodules to be formed on evaporation (Berlin).

Zinc cyanides. $ZnCy_2$ is known, and also several double cyanides.

Zinc cyanide $ZnCy_2$. Obtained by adding KCNAq (free from K_2CO_3) to solution of a Zn salt, or by adding HCNAq to Zn acetate solution. Special precautions are needed to insure production of pure $ZnCy_2$ (*v.* Wöhler, *B. J.* 20, 152; Oppermann, *J.* 1860. 226; Joannis, *C. R.* 92, 1338, 1417; Rammelsberg, *P.* 42, 114). $ZnCy_2$ is obtained in crystals by covering a layer of conc. $Zn(C_2H_3O_2)_2Aq$ with a little water, and very carefully pouring on to this dilute HCNAq; the crystals form slowly. Crystallises in orthorhombic prisms. The pp. by KCN and HCN is white with a tinge of yellow. Decomposed by strongly heating, giving off Cy (Rammelsberg). Insol. water and alcohol; e. sol. alkalis and KCNAq; sl. sol. in conc. solutions of Zn salts (Joannis). With hot KOHAq it forms $K_2O.ZnO$ and $ZnCy_2.2KCy$. H.F. $[Zn,Cy^2] = 58,600$; $[ZnO,2HCyAq] = 13,400$ (Joannis).

Double cyanides containing $ZnCy_2$.—These compounds are obtained by dissolving $ZnCy_2$ in a solution of the other cyanide and crystallising:—

$ZnCy_2.2NH_4Cy$ (Corriol a. Berthemot, *J. Ph.* 16, 414).

$ZnCy_2.BaCy_2.2H_2O$ (Weselsky, *B.* 2, 588).

$ZnCy_2.CaCy_2.xH_2O$ (Schindler, *Magaz. Pharm.* 36, 70).

$ZnCy_2.2KCy$ (Gmelin; Fresenius a. Haidlen, *A.* 43, 132). $[Zn,Cy^2,2KCyAq] = 62,230$ (*Th.* 3, 475).

$ZnCy_2.2NaCy.5H_2O$ (Rammelsberg, *P.* 42, 112).

$ZnCy_2.HgCy_2.HgCl_2.6H_2O$ (Varet, *C. R.* 106, 1080).

$ZnCy_2.HgCy_2.HgCl_2.6NH_3$ (Varet, *l.c*).

SELENOCYANIDES. *Salts of selenocyanhydric acid* HSeCy. Also called *selenocyanates.* Discovered by Berzelius in 1820 (*S.* 31, 60); more fully examined by Crookes (*C. J.* 4, 12).

Selenocyanhydric acid HSeCyAq. (*Seleno-, or seleno-cyanic acid. Hydrogen seleno- or seleno-cyanate. Hydroselenocyanic acid.*) Known only in solution; prepared by passing a rapid stream of H_2S through hot $Pb(SeCy)_2Aq$ containing $Pb(SeCy)_2$ in suspension, filtering from PbS, heating the filtrate nearly to boiling, and filtering again (if necessary) from ppd. Se. This solution, which is markedly acid, is decomposed on boiling; it cannot be concentrated without change even over H_2SO_4 *in vacuo.* It is decomposed by acids into HCy and Se. The solution dissolves Zn and Fe with evolution of H (Crookes, *C. J.* 4, 12).

Ammonium selenocyanide $NH_4.SeCy$. By neutralising HSeCyAq by NH_3Aq and evaporating. Soluble, deliquescent, crystallises in minute needles (Crookes, *l.c.*).

Barium, Calcium, and Strontium selenocyanides $M(SeCy)_2$ [M = Ba, Ca, or Sr]. By dissolving MCO_3 in HSeCyAq and concentrating *in vacuo* (Crookes).

Copper selenocyanide. Brown pp. by adding KSeCyAq to $CuSO_4Aq$; very soon decomposes to HSeCyAq and CuSe (C.).

Gold selenocyanide. Not isolated. When an alcoholic solution of KSeCy is added to $AuCl_3Aq$, Se is ppd., and the filtrate on evaporation yields small dark-red prisms of the *double salt* $AuK(SeCy)_2$ (Clarke, *B.* 11, 1326)

Iron selenocyanide. Not isolated. Crookes (*l.c.*) mentions various reactions which do not yield a definite salt.

Lead selenocyanide $Pb(SeCy)_2$. By adding KSeCyAq to Pb acetate solution, dissolving the pp. in boiling water, filtering (if necessary), and crystallising. Lemon-coloured needles; insol. alcohol; not changed at 100° (C.).

Magnesium selenocyanide. By dissolving $MgCO_3$ in HSeCyAq and evaporating; a gummy non-crystallisable mass; composition undecided.

Mercury selenocyanide. Two salts have been isolated, $Hg(SeCy)_2$ and HgSeCy (Cameron a. Davy, *Tr. Irish Acad.* 27, 148).

Mercuric selenocyanide $Hg(SeCy)_2$; a greyish white salt obtained by adding KSeCyAq to $Hg(C_2H_3O_2)_2Aq$. Soluble in $HgCl_2Aq$, forming $Hg(SeCy)_2.HgCl_2$. Not obtained by using $HgCl_2$ in place of $Hg(C_2H_3O_2)$ (Crookes).

Mercurous selenocyanide HgSeCy; olive green, amorphous; by ppg. $HgNO_3Aq$ by KSeCyAq.

Platinum selenocyanide. Not isolated. Addition of $PtCl_4Aq$ to an alcoholic solution of KSeCy forms a reddish pp.; when this is treated with boiling water part of it dissolves, and the filtrate gives crystals on cooling; these crystals are dissolved in alcohol and re-crystallised; they are the *double salt* $K_2Pt(SeCy)_6$; S.G. 3·377 at 10·2°, 3·378 at 12·5° (Clarke, *Am. S.* 16, 119).

Potassium selenocyanide KSeCy. Prepared by dissolving red Se (ppd. in the cold) in KCyAq and evaporating (Schiellerup, *A.* 109, 125). Also by fusing 1 part Se with 3 parts dry K_4FeCy_6 in a small retort, digesting with absolute alcohol, passing CO_2 through the liquid to decompose KCy and KNCO and ppt. $KHCO_3$, distilling off the alcohol, dissolving in water, filtering, and crystallising *in vacuo* over H_2SO_4 (C.). White, needle-shaped deliquescent crystals; melt without change, if out of contact with air (Berzelius); in air decomposes a little above 100° (C.). $KSeCy_6Aq$ is alkaline to litmus; decomposed by acids with evolution of HCy and ppn. of Se. Cl produces CyCl and Se (*cf.* Kypke a. Neger, *A.* 115, 207). Several double compounds are described by Cameron a. Davy (*Tr. Irish Acad.* 27, 151); $X.HgCy_2$, $X.HgBr_2$, $X.HgI_2$, $X.HgCl_2$, $X.Hg(SCy)_2$.

Silver selenocyanide AgSeCy. Ppd. on adding $AgNO_3Aq$ to KSeCyAq; if NH_4Aq is present pp. separates in small shining crystals. Blackens in light; insol. in water; sparingly sol. in cold dilute acids; decomposed by hot conc. acids (C.).

Sodium selenocyanide NaSeCy. Small crystals; by neutralising HSeCyAq by Na_2CO_3, and evaporating *in vacuo* (C.).

Zinc selenocyanide. Non-deliquescent crystals [$?Zn(SeCy_2)_2$]; by dissolving Zn or ZnO in HSeCyAq and evaporating (C.).

SULPHOCYANIDES. (*Rhodanides. Sulphocyanates. Thiocyanates.*) *Salts of sulphocyanic acid* HSCN. For an account of sulphocyanic acid *v.* CYANIC (SULPHO) ACID, p. 303; and for general properties of sulphocyanides *v.* p. 328. *Disulphocyanides* (salts of $H_2C_2N_2S_3$) are described in the art. CYANURATES (METALLIC) and SULPHOCYANURATES, p. 360.

Aluminium sulphocyanide $Al_2O_3.xH_2O$ dissolves slowly in HSCyAq; when the solution is evaporated over H_2SO_4 a gummy mass is obtained, which may be the neutral salt; if the solution is evaporated at 100° H_2S and HCy are evolved and yellow flakes (? basic salt) separate (Meitzendorff, *P.* 56, 63).

Ammonium sulphocyanide NH_4SCy. H.F. $[N, H^4, S, Cy] = 59,100$ (Joannis, *A. Ch.* [5] 26, 540). Produced by decomposing $Cu(SCy)_2$ by NH_4HSAq, filtering, and evaporating; also by evaporation of NH_4Aq mixed with alcoholic solution of CS_2 (Millon, *Z.* 1861. 64; Zeise, *A.*

47, 36; Claus, *A.* 179, 112). Prepared by digesting the HCNAq from 6 parts K_4FeCy_6 (by distilling with 3 parts conc. H_2SO_4 mixed with $1\frac{1}{3}$ parts water) with the NH_4 polysulphide solution obtained by saturating 2 parts NH_3Aq, S.G. ·95, with H_2S, and adding 2 parts of the same NH_3Aq and 2 parts S.; the liquid is boiled till all NH_4 sulphide is decomposed with separation of S, filtered, evaporated, and crystallised (about $1\frac{1}{3}$ to $1\frac{2}{3}$ parts NH_4SCy are obtained) (Liebig, *A.* 61, 126). Large, white, deliquescent plates. S.G. 1·3075 at 13° (Clarke, *J.* 1877. 43). V. sol. water and alcohol; melts at 159° (Reynoso, *A.* 150, 255); and at higher temperature (180°–190°) evolves CS_2, H_2S, and NH_3, and leaves guanidin sulphocyanide (Volhard, *B.* 7, 92; Delitsch, *J. pr.* [2] 8, 240; 9, 1); at 230°–250° thioprussiamic acids are formed (Claus a. Seippel, *B.* 7, 92); at still higher temperature mellam is formed, and finally mellone (Volhard, *J. pr.* [2] 9, 28). Heated for some time nearly to its M.P., thio-urea, $CS(NH_2)_2$ (isomeric with NH_4SCy), is produced (Volhard, *B.* 7, 92; Reynoso, *A.* 150, 255). S. 122·1 at 0°, 162·2 at 20°; much heat disappears during solution (Rudorff, *B.* 2, 68; Clowes, *Z.* 1866. 190; Joannis, *A. Ch.* [5] 26, 482). Several metallic oxides, *e.g.* HgO, ZnO, Ag_2O, dissolve in $NH_4.SCyAq$ and form double sulphocyanides (Fleischer, *A.* 179, 225). Combines with $HgCy_2$ to form the *double compound* $NH_4SCy.HgCy_2$ (Clève, *Bl.* [2] 23, 71).

Arsenic sulphocyanide $As(SCy)_3$. Produced in very small quantity by heating together $AsCl_3$ and $Pb(SCy)_2$; volatile at c. 400° forming oily drops which solidify to crystals; insol. in all ordinary menstrua; decomposed by water to As_2O_3Aq and HSCy (Miguel, *A. Ch.* [5] 11, 341).

Barium sulphocyanide $Ba(SCy)_2.2H_2O$. Formed by neutralising HSCyAq by $BaCO_3$, evaporating at 100°, and then over H_2SO_4 (Meitzendorff, *P.* 56, 63). Long, lustrous, deliquescent needles; v. sol. alcohol and water. From warm solution of this salt mixed with warm $HgCy_2Aq$ the *double compound* $Ba(SCy)_2.HgCy_2.4H_2O$ separates on cooling (Clève, *Bl.* [2] 23, 71; *cf.* Storck a. Strobel, *D. P. J.* 235, 156).

Beryllium sulphocyanide [? $Be(SCy)_2$]. Prepared by adding $BeSO_4$ to $Ba(SCy)_2Aq$ (Toczynsky, *Z.* 1871. 276); or by dissolving $BeCO_3$ in HSCyAq and crystallising (Hermes, *J. pr.* 97. 465).

Bismuth sulphocyanide $Bi(SCy)_3$. By dissolving $Bi_2O_3.xH_2O$ in HSCyAq, evaporating, filtering from the yellow basic salt which separates, and evaporating again; dark orange red powder (Meitzendorff, *P.* 56, 63).

Cadmium sulphocyanide $Cd(SCy)_2$. White crystals; sp. sol. water; by dissolving $CdCO_3$ in HSCyAq and evaporating (Meitzendorff, *P.* 56, 63). By dissolving this salt in NH_3Aq, and evaporating with frequent addition of NH_3Aq, the *double compound* $Cd(SCy)_2.2NH_3$ is formed (M.). The *double compound* $Cd(SCy)_2.2HgCy_2.4H_2O$ is described by Clève (*Bl.* [2] 23, 71).

Calcium sulphocyanide $Ca(SCy)_2.3H_2O$. Prepared like the Ba salt. Crystallises badly; sol. water (Meitzendorff, *P.* 56, 63). From hot solutions of this salt and $HgCy_2$ the *double compound* $Ca(SCy)_2.2HgCy_2.8H_2O$ crystallises on cooling (Clève, *Bl.* [2] 23, 71; Böckmann, *A.* 22, 153).

Cerium sulphocyanide $Ce(SCy)_3.7H_2O$; *double compound* $Ce(SCy)_3.3HgCy_2.12H_2O$ (Jolin, *Bl.* [2] 21, 535).

Chromium sulphocyanides. Besides *chromic sulphocyanide*, the acid *chromisulphocyanhydric*, $H_3Cr(SCy)_6$, is known in aqueous solution, and a series of salts, *chromisulphocyanides*, is derived from it; there are also several *chrom-ammonium sulphocyanides* known.

Chromic sulphocyanide $Cr(SCy)_3$. Dark-green, amorphous, deliquescent mass, obtained by dissolving $Cr_2O_3.xH_2O$ in HSCyAq, and evaporating over H_2SO_4 *in vacuo* (Clasen, *J. pr.* 96, 319).

Chromisulphocyanhydric acid, or *chromisulphocyanic acid*, $H_3Cr(SCy)_6Aq$; known only in aqueous solution, which is obtained by decomposing the Pb or Ag salt by H_2S. The solution is dark wine-red and distinctly acid; it decomposes on evaporation to HSCyAq and $Cr(SCy)_3$ (Rosler, *A.* 141, 185).

Potassium chromisulphocyanide $K_3Cr(SCy)_6.4H_2O$. Prepared by heating for about 2 hours a fairly conc. solution of 6 parts KSCy and 5 parts chrome-alum, ppg. by alcohol, filtering, and crystallising from alcohol. Forms almost black crystals, which appear ruby red by transmitted light; loses all H_2O at 110°. Solution of this salt is not ppd. by alkali carbonates or by NH_4HS; it is ppd. by NaOHAq only on heating; evaporated with HClAq, KCl and $CrCl_3$ are produced (Rosler, *A.* 141, 185). Besides the K salt the following are described by Rosler (*l.c.*):—
$(NH_4)_3Cr(SCy_6).8H_2O$; $Ba_3 2Cr(SCy)_6.16H_2O$; $Pb_3 2Cr(SCy)_6.4Pb(OH)_2.8H_2O$; $Ag_3Cr(SCy)_6$; $Na_3Cr(SCy)_6.7H_2O$.

Chrom-ammonium sulphocyanides. The composition of these salts may be expressed by the formula $2Cr(SCy)_3.4NH_3.M^{II}(SCy)_2$ where $M = 2NH_4$, K_2, Ag, Cu_2, or Hg; these salts do not seem to be double compounds, but rather salts of the complex acid $H_2(SCy)_8(N_4H_{10}Cr_2)$. The acid itself is known in aqueous solution; it is obtained by decomposing the Hg salt by H_2S; the solution is deep-red, by careful evaporation a red amorphous mass is obtained (Reinecke, *A.* 126, 113).

The *ammonium salt* $(NH_4)_2(SCy)_8(N_4H_{10}Cr_2)$ is obtained by adding powdered $K_2Cr_2O_7$ to molten NH_4SCy until the mass becomes solid, treating with hot water, and adding pieces of NH_4Cl to the deep-red liquid, when the salt separates in reddish crystals. V. sol. alcohol and ether; by prolonged treatment with water it forms NH_4SCy, $Cr(SCy)_3$, and Cr_2O_3; easily decomposed by dilute acids or alkalis (Reinecke, *A.* 126, 113; *cf.* Morland, *J.* 1860. 162).

The *potassium salt* $K_2(SCy)_8(N_4H_{10}Cr_2)$ is obtained by reacting on the NH_4 salt by conc. KOHAq, and re-crystallising the compound which separates from hot water.

The *sodium salt* is obtained by a similar process, using NaOHAq. The soluble salts give pps. with salts of many heavy metals; the following have been isolated:—
$Cu_2(SCy)_8(N_4H_{10}Cr_2)$, $Hg(SCy)_8(N_4H_{10}Cr_2)$, $Ag_2(SCy)_8(N_4H_{10}Cr_2)$.

Cobalt sulphocyanide $Co(SCy)_2$ (Claus, *A.* 99, 48). Obtained by dissolving $CoO.xH_2O$ in

HSCyAq, and evaporating. According to Meitzendorff (*P.* 56, 63) the salt crystallises with $\frac{1}{2}H_2O$. Solution in water is rose-red, becoming deep blue by concentration. Alcoholic or ethereal solution becomes blue on dilution; this reaction has been applied for the optical determination of Co (Wolff, *Fr.* 1879. 38). The *double compound* $Co(SCy)_2.Hg(SCy)_2$ is known (Clève, *J. pr.* 91, 227; Skey, *J.* 1874. 300).

Copper sulphocyanides. *Cuprous sulphocyanide* $Cu_2(SCy)_2$ (Meitzendorff, *P.* 56, 63). Formed by adding KSCyAq to $CuSO_4Aq$ reduced by $FeSO_4$ or SO_2. White powder, insol. water and dilute acids; sol. NH_3Aq. May be used in quantitative estimation of Cu (Rivot, *C. R.* 38, 868; Busse, *Fr.* 1878. 55). *Cupric sulphocyanide* $Cu(SCy)_2$ (Meitzendorff, *l.c.*; Hull, *A.* 76, 93). Black crystalline powder; by adding KSCyAq to fairly air-free conc. $CuSO_4Aq$ containing a little H_2SO_4; decomposed by water, quickly when hot, to $Cu_2(SCy)_2$, HSCy, HCy, and H_2SO_4. Dissolves in NH_3Aq, and gives the *double salt* $Cu(SCy)_2.2NH_3$ (Meitzendorff, *l.c.*).

Didymium sulphocyanide $Di(SCy)_3.6H_2O$ (Clève, *Bl.* [2] 21, 248).

Erbium sulphocyanide $Er(SCy)_3.6H_2O$ (Clève a. Hoeglund, *Bl.* [2] 18, 197). *Double compound* $Er(SCy)_3.3HgCy_2.12H_2O$ (Clève, *Bl.* [2] 21, 344).

Gold sulphocyanides; known only in combination.

Aurous-potassium sulphocyanide AuSCy.KSCy. $AuCl_3Aq$ is added drop by drop to KSCyAq at 80° as long as the pp. dissolves, the liquid is evaporated and crystallised. Straw-yellow prisms; melts at 100°; decomposed by heat to S, CS_2, Au, and KSCy. Solution blackens in light; it gives pps. with salts of many heavy metals (Clève, *J. pr.* 94, 14). Addition of NH_3Aq pps. the *double compound* $AuSCy.NH_3$.

Auric-potassium sulphocyanide $Au(SCy)_3.KSCy$. $AuCl_3Aq$ is added to excess of KSCyAq in the cold (Clève, *J. pr.* 94, 14). Crystallises from warm water in orange-red needles; sol. alcohol and ether. Forms *double compounds* (Skey, *J.* 1874. 300).

Auric-sodium sulphocyanide $Au(SCy)_3.NaSCy$ (Kern, *J.* 1876. 319).

Iron sulphocyanide. *Ferric sulphocyanide* $Fe(SCy)_3.1\frac{1}{2}H_2O$; by KSCyAq to $FeCl_3Aq$ and evaporating. Small blackish-red crystals; v. sol. water, alcohol, and ether. Solution is decolourised by $NaHCO_3$ with ppn. of all Fe; not decolourised by HClAq (Clève, *J. pr.* 91, 227; *cf.* Skey, *J.* 1874. 300). *Ferrous sulphocyanide* $Fe(SCy)_2.1\frac{1}{2}H_2O$. Greenish prisms, by adding KSCyAq to $FeSO_4Aq$; v. sol. water, alcohol, and ether; unstable (Claus, *A.* 99, 48). Forms a *double compound* $Fe(SCy)_2.Hg(SCy)_2$ (Clève, *J. pr.* 91, 227).

Lanthanum sulphocyanide $La(SCy)_3.7H_2O$. *Double compound* $La(SCy)_3.3HgCy_2.12H_2O$ (Clève, *Bl.* [2] 21, 196).

Lead sulphocyanide $Pb(SCy)_2$. Yellow lustrous monoclinic crystals; by ppg. neutral $Pb(C_2H_3O_2)Aq$ by KSCyAq. S.G. 3·82 (Schabus, *W. A. B.* 1850. 108). Decomposed by hot water to the *basic salt* PbOH.SCy, which is also obtained by adding basic Pb acetate to KSCyAq (Liebig, *P.* 25, 546). H.F. [Pb, S, Cy] = 23,000 (Joannis, *A. Ch.* [5] 26, 540). The *double salts* $Pb(SCy)_2.PbBr_2$, $Pb(SCy)_2.8PbBr_2$, and $3Pb(SCy)_2.PbI_2$. are described by Thorp (*Am.* 10, 229).

Lithium sulphocyanide LiSCy (Hermes, *J. pr.* 97, 465).

Magnesium sulphocyanide $Mg(SCy)_2.4H_2O$. White deliquescent crystals; by dissolving $MgCO_3$ in HSCyAq and evaporating (Meitzendorff, *P.* 56, 63). Forms the *double compound* $Mg(SCy)_2.2HgCy_2.4H_2O$ by mixing warm solutions of the two salts and allowing to cool (Clève, *Bl.* [2] 23, 71).

Manganese sulphocyanide $Mn(SCy)_2.3H_2O$ (Meitzendorff, *P.* 56, 63). By dissolving $MnCO_3$ in HSCyAq and evaporating. Loses $3H_2O$ at 160°–170°.

Mercury sulphocyanides. *Mercurous sulphocyanide* HgSCy (Wohler, *G. A.* 69, 271). H. F. [Hg, S, Cy] = 18,000 (Joannis, *A. Ch.* [5] 26, 540). White pp. by adding dilute KSCyAq to a large excess of very dilute $HgNO_3Aq$ with a little HNO_3 added; if the solutions are not dilute the pp. is grey and contains Hg (Claus, *J. pr.* 15, 401; Hermes, *J. pr.* 97, 465). Sol. in hot HClAq, also in KSCyAq, with separation of Hg (Philipp, *P.* 131, 86). *Mercuric sulphocyanide* $Hg(SCy)_2$. White pp. by mixing $HgCl_2Aq$ or $Hg(NO_3)_2Aq$ and KSCyAq; sol. excess of either salt; v. sl. sol. water, m. sol. alcohol; soluble with decomposition in solutions of chlorides. When $Hg(SCy)_2$ is heated it swells up, giving off Hg vapour, N, and CS_2, and leaving a grey mass like graphite, and at a higher temperature forming mellon. This salt is sold under the name of '*Pharaoh's serpents.*' (Hermes, *J. pr.* 97, 465; Philipp, *P.* 131, 86.) $Hg(SCy)_2$ dissolves in some other sulphocyanides forming *double sulphocyanides*; the following have been isolated:—$Hg(SCy)_2.2NH_4SCy$ (Fleischer, *A.* 179, 225); $Hg(SCy)_2.2KSCy$ (Hermes, *J. pr.* 97, 465); $Hg(SCy)_2.Zn(SCy)_2$ (Clève, *J. pr.* 91, 227). Besides these double sulphocyanides $Hg(SCy)_2$ forms several *double compounds* with other salts; $Hg(SCy)_2.3NH_3.H_2O$ (Fleischer, *A.* 179, 225); $Hg.SCy.NH_2.HgO$ (Claus, *J. pr.* 15, 401; Philipp, *P.* 131, 86; Fleischer, *l.c.*); $Hg(SCy)_2.3HgO$ (Fleischer, *l.c.*); $Hg.SCy.C_2H_3O_2$ (Byk, *J. pr.* [2] 20, 328); $Hg(SCy)_2.KCy.2H_2O$ (Bockmann, *A.* 22, 153; Claus, *l.c.*; Philipp, *l.c.*).

Molybdenum sulphocyanide. Pp. formed by adding conc. KSCyAq to a Mo salt is probably $Mo(SCy)_3$ (?). Sol. in water or ether with intense dark carmine red colour (Braun, *Fr.* 1863. 36; 1867. 86). Said to form a double compound with $Hg(SCy)_2$ (Skey, *C. N.* 30, 25).

Nickel sulphocyanide $Ni(SCy)_2.\frac{1}{2}H_2O$; yellow crystalline powder; obtained by evaporating solution of NiO in HSCyAq (Meitzendorff, *P.* 56, 63). Dissolves in NH_3Aq, and solution evaporated on water-bath gives blue efflorescent crystals of the *double compound* $Ni(SCy)_2.4NH_3$; decomposed by water to NH_3Aq and NiO (Meitzendorff, *l.c.*). Also forms a *double compound* with $Hg(SCy)_2$, viz. $Ni(SCy)_2.Hg(SCy)_2.2H_2O$ (Clève, *J. pr.* 91, 227).

Palladium sulphocyanides. None certainly isolated; if a simple sulphocyanide of Pd exists it is very soluble in water (*v.* Porrett, *T.* 1814. 527). By dissolving $PdCl_2.2KCl$ and KSCy in water and crystallising, a double sulphocyanide of Pd and K is obtained; other double palladium sulphocyanides are also said to be formed by reactions similar to those whereby sulphocyano-platinum compounds are produced; the composition of these salts is not yet finally decided, the data are meagre (*v.* Croft, *C. N.* 16, 53).

Phosphorus sulphocyanide $P(SCy)_3$ *v.* PHOSPHORUS.

Platinum sulphocyanides. The reddish-brown solid obtained in the reaction between some of the double Pt sulphocyanides, *e.g.* $K_2Pt(SCy)_6$ and Cl or HNO_3Aq, is probably *platinous sulphocyanide*, $Pt(SCy)_2$ (Buckton, *C. J.* 7, 22). *Platinic sulphocyanide* has not been isolated. Many double compounds of $Pt(SCy)_2$ and $Pt(SCy)_4$ are known, but they are better regarded as salts of the acids $H_2Pt(SCy)_4$ and $H_2Pt(SCy)_6$, both of which are known in aqueous solution; the salts in question are generally called *sulphocyano-platinites* and *sulphocyano-platinates*, or sometimes *platinoso-* and *platino- sulphocyanides*. The K salts are formed by reaction between KSCy and $PtCl_2Aq$ or $PtCl_4Aq$; the salts of the heavy metals are formed from the K salts by double decomposition. Both series of salts are decomposed by Cl or HNO_3Aq with formation of HCy, H_2SO_4(HCl), $K_2SO_4(KNO_3)$, and separation of a brownish-red solid which is probably $Pt(SCy)_2$. NH_3Aq reacts with salts of both series to form *platosammonium sulphocyanide* $(N_2H_6Pt).2SCy$ (*q. v.*). The sulphocyano-platinum compounds have been chiefly investigated by Buckton (*C. J.* 7, 22).

Sulphocyanoplatinous acid $H_2Pt(SCy)_4Aq$. (*Platinoso-sulphocyanic acid. Platinoso-sulphocyanhydric acid.*) Known only in aqueous solution, which is obtained by carefully adding dilute H_2SO_4Aq to the Ba salt; the solution soon decomposes even by evaporation *in vacuo*, giving HSCyAq and a pp. containing Pt.

Ammonio-platinous sulphocyano-platinite or *platinoso-sulphocyanide* $(N_4H_{12}Pt).Pt(SCy)_4$. (*Diammonio-platosammonium sulphocyano-platinite*, $(N_2H_4[NH_3]_2Pt).Pt(SCy)_4$.) Obtained by adding KSCyAq to diplatosammonium chloride, $N_2H_4[NH_3]_2Pt_2.Cl_2$; buff pp.; insol. in water and alcohol, sol. in dilute HClAq; when heated it is decomposed, burning like tinder, and leaves Pt. This salt seems to be polymeric with *platosammonium sulphocyanide*, $(N_2H_6Pt).2SCy$ (*q. v.*).

Potassium sulphocyanoplatinite or *platinoso-sulphocyanide* $K_2Pt(SCy)_4$. Prepared by dissolving equal parts of $PtCl_2$ and KSCy in as small a quantity as possible of hot water, and crystallising from alcohol the salt which separates. Also by adding $PtCl_2.2KCl$ in small successive quantities to conc. KSCyAq, crystallising from alcohol, pressing between paper, and re-crystallising from water. Red microscopic crystals; six-sided prisms; S. 40 at 15·5°; v. sol. in alcohol. Non-deliquescent; not changed at 100° if dry; decomposed by NH_3Aq to $(N_2H_6Pt).2SCy$ and KSCyAq.

Silver sulphocyano-platinite or ***platinoso-sulphocyanide*** $Ag_2Pt(SCy)_4$. White curdy pp. by adding $AgNO_3Aq$ to solution of the K salt. Partly soluble in NH_3Aq with decomposition; sol. in KSCyAq.

Sulpho-cyanoplatinic acid or ***platino-sulphocyanic acid*** (*Platino-sulphocyanhydric acid*) $H_2Pt(SCy)_6Aq$. Known only in aqueous solution, which is obtained by decomposing the Pb salt by H_2S; decomposes when evaporated, even *in vacuo*; dark-red liquid with acidic taste; decomposes carbonates and dissolves Zn evolving H.

Ammonium sulphocyanoplatinate or *platino-sulphocyanide* $(NH_4)_2Pt(SCy)_6$. Carmine-red six-sided tables; formed by boiling 1 part $(NH_4)_2SO_4$ with 1½ parts $K_2Pt(SCy)_6$ in conc. solution, separating $(NH_4)_2SO_4$ and K_2SO_4 by adding alcohol, and re-crystallising the salt from warm water. Aqueous solution is decomposed by boiling, giving off HSCy.

Barium sulphocyanoplatinate or *platino-sulphocyanide* $BaPt(SCy)_6$. Red needles; sol. in water and alcohol; by reaction between excess of $BaCl_2Aq$ and $K_2Pt(SCy)_6$, evaporating and dissolving in alcohol.

Cupric sulphocyanoplatinate or *platino-sulphocyanide*; green pp. by adding $K_2Pt(SCy)_6Aq$ to $CuSO_4Aq$, probably $CuPt(SCy)_6$; becomes black when liquid is boiled; sol. in NH_3Aq, reppd. by HClAq.

Iron sulphocyanoplatinates or *platino-sulphocyanides*. The *ferrous salt* $FePt(SCy)_6$ is a black crystalline pp., insol. in water and alcohol, obtained by adding slightly acidulated $FeSO_4Aq$ to conc. $K_2Pt(SCy)_6Aq$. The *ferric salt* is prepared by using $FeCl_3Aq$ in place of $FeSO_4Aq$ and boiling; probably $Fe_2 2Pt(SCy)_6$.

Lead sulphocyanoplatinate or *platino-sulphocyanide* $PbPt(SCy)_6$; golden-yellow hexagonal plates, obtained by mixing conc. $Pb(C_2H_3O_2)_2Aq$ and conc. $K_2Pt(SCy)_6$, washing with cold water, and crystallising from alcohol; decomposed by hot water. The *basic salt* $PbPt(SCy)_6.PbO$ is formed as a red pp. by ppg. basic Pb acetate solution with conc. $K_2Pt(SCy)_6Aq$.

Mercurous sulphocyanoplatinate or *platino-sulphocyanide* $Hg_2Pt(SCy)_6$; yellow pp. by adding $HgNO_3Aq$ to $K_2Pt(SCy)_6Aq$.

Potassium sulphocyanoplatinate or *platino-sulphocyanide* $K_2Pt(SCy)_6$. Prepared by adding 2 pts. K_2PtCl_6 to a warm solution of 2½ pts. KSCy, heating nearly to boiling, filtering, and allowing to crystallise; the crystals are dissolved in boiling alcohol (to separate KCl), and the liquid is passed through a filter which is kept warm. Also produced by adding $PtCl_4Aq$ to conc. KSCyAq at 70°-80°, and allowing to cool. Deep carmine-red, six-sided prisms; permanent in air at ordinary temperatures; S. c. 8½ at 60°, S. much greater at 100°. Crystallises with $2H_2O$ according to Gmelin (*cf.* Wyrubow, *Bl.* [2] 33, 402). Heated to redness gives KSCy, Pt, and gaseous products. Decomposed by hot H_2SO_4 or HClAq. With HNO_3Aq or Cl probably gives $Pt(SCy)_2$. Reacts with NH_3Aq or $(NH_4)_2CO_3Aq$ to form K_2SO_4, KSCy, NH_4Cy, NH_4SCy, and ppt. yellow needles of platosammonium sulphocyanide $(N_2H_6Pt).2SCy$ (*q. v.*).

Silver sulphocyanoplatinate or *platino-sulphocyanide* $Ag_2Pt(SCy)_6$. Orange-yellow pp. by mixing $AgNO_3Aq$ with $K_2Pt(SCy)_6Aq$. Forms a *double salt* $Ag_2Pt(SCy)_6.2KSCy$.

Sodium sulphocyanoplatinate or ***platino-sulphocyanide*** $Na_2Pt(SCy)_6$. Garnet-coloured tablets; obtained by decomposing the Pb salt by Na_2SO_4Aq; sol. water and alcohol.

Platosammonium sulphocyanide $(N_2H_6Pt).2SCy$. This salt is obtained by decomposing potassium platino-sulphocyanide $K_2Pt(SCy)_6$ (*v. supra*) by NH_3Aq or $(NH_4)_2CO_3Aq$, collecting the crystals which separate, washing them with cold water, and recrystallising from alcohol. It is also produced when NH_3Aq reacts with potassium platinoso-sulphocyanide $K_2Pt(SCy)_4$, or by mixing 1 pt. KSCy with 1·6 pts. platosammonium chloride $N_2H_6PtCl_2$ in aqueous solution, heating nearly to boiling, adding an equal volume of alcohol, filtering hot, and allowing to cool. Straw-yellow needles; melts at 100°–110°; decomposes at c. 180°, giving off NH_3 and HCy, and also SO_2 if in air, and leaving Pt. Sparingly sol. cold water, more sol. alcohol. Not acted on by dilute HClAq or H_2SO_4Aq. Aqueous solution is decomposed on boiling, evolving NH_3 (Buckton, *C. J.* 7, 22). The salt described as *ammonio-platinous platinoso-sulphocyanide* $(N_2H_4[NH_4]_2Pt).Pt(SCy)_4$ (*v.* p. 351) is probably polymeric with platosammonium sulphocyanide.

Potassium sulphocyanide KSCy. H.F. [K,S,Cy] = 87,800 (Joannis, *A. Ch.* [5] 26, 482).

Formation.—1. By fusing 1 pt. dry K_4FeCy_6 with 3 pts. $K_2S_2O_3$ (Frohde, *P.* 119, 317).—2. By heating NH_4SCy with KOHAq, or $(NH_4)_2CS_3$ with K_2SAq (Gélis).—3. By adding a mixture of S, C, and $(NH_4)_2SO_4$ to a molten mixture of KOH and S (Fleck, *D. P. J.* 169, 209) $[(NH_4)_2SO_4 + C + S = NH_4.SCy + SO_2 + 2H_2O$; and $2NH_4SCy + K_2S = 2KSCy + (NH_4)_2S]$.—4. An aqueous solution of KCy (65 pts.) is digested with S (32 pts.) until S is all dissolved (Wiggers, *A.* 29, 319).

Preparation.—A mixture of 32 pts. S with 17 pts. K_2CO_3 is heated until it melts, 46 pts. dry K_4FeCy_6 are added, and heating is continued until the mass fuses quietly and a little taken out does not give the reactions of ferrocyanide; temperature is then raised for a little to change any $K_2S_2O_3$ into K_2SO_4; the cold mass is extracted with water, and the liquid is neutralised by H_2SO_4Aq; the liquor is evaporated to dryness, the residue is boiled with alcohol, the alcoholic solution is filtered and crystallised (Henneberg, *A.* 73, 230; *cf.* Liebig, *A.* 50, 345; 51, 288; Babcock, *Z.* 1866. 666; Frohde, *P.* 119, 317).

Properties.—Long, white, striated prisms, resembling nitre. S.G. 1·886–1·906 (Bodeker, *J.* 1860. 17). S. 177·2 at 0°, 217 at 20° (Rudorff, *B.* 2, 68). By dissolving 150 pts. of the salt in 100 pts. water at 10·8°, temperature falls to −23·7° (Rudorff, *B.* 2, 68). Joannis (*A. Ch.* [5] 26, 482) gives the heat of solution [KSCy,Aq] = −6100. Melts at 161·2° (Pohl, *J.* 1851. 59). The molten salt becomes brown, then green, finally indigo blue, but on cooling it again goes white (Nöllner, *P.* 98, 189). Non-poisonous (Wohler a. Frerichs, *A.* 65, 342; Hermes, *J. pr.* 97, 465). According to Berzelius (*S.* 31, 42), when KSCy is heated in moist air it evolves CO_2 and NH_3 and K_2S remains. KSCyAq slowly decomposes, quickly on boiling, evolving NH_3 (Vogel, *S.* 23, 15).

Reactions.—1. *Chlorine* passed into melted KSCy forms S_2Cl_2 and Cy_3Cl_3 (Liebig, *P.* 15, 548; 34, 576). Cl passed into fairly conc. KSCyAq forms pseudosulphocyanogen $C_3N_3HS_3$; with excess of Cl, NH_3, H_2SO_4, HCl, and CO_2 are produced (Liebig, *A.* 39, 215; 50, 337; Völckel, *A.* 43, 97; Parnell, *P. M.* 17, 249).—2. Conc. *nitric acid* ppts. $C_3N_3HS_3$ (Liebig; Volckel).—3. *Potassium permanganate*, *manganese dioxide*, or *lead peroxide* oxidises the S of KSCy to H_2SO_4 (Hadow, *C. J.* 11, 174).—4. Molten KSCy reacts violently with *hydrochloric acid gas*, forming HCy, CS_2, and NH_4Cl (Liebig, *l.c.*).—5. Heated gently with *phosphorus pentachloride* CyCl, KCl, and $PSCl_3$ are produced; at a higher temperature the products vary (Schiff, *A.* 106, 116).—6. Heated with *iron* FeS, K_2S, and K_4FeCy_6 are formed (Gélis, *Rep. Chim. App.* 1862. 370).—7. KSCyAq *electrolysed* gives H_2SO_4, SO_2, HCy and S (Schlagdenhauffen, *J. Ph.* [3] 49, 100).

Combinations.—With *mercuric cyanide* and *iodide* to form $KSCy.HgCy_2.2H_2O$ (Bockmann, *A.* 22, 153; Clève, *Bl.* [2] 23, 71; Philipp, *P.* 131, 86): $2KSCy.HgI_2.2H_2O$ (Philipp, *l.c.*).

Silicon sulphocyanide $Si(SCy)_4$ *v.* SILICON.

Silver sulphocyanide AgSCy. H.F. [Ag,S,Cy] = 16,500 (Joannis, *A. Ch.* [5] 26, 540). White curdy pp. by adding KSCyAq to $AgNO_3Aq$. Blackens in light. Insol. water and dilute acids; sol. NH_3Aq and alkali sulphocyanides, also in $HgNO_3Aq$ (Wackenroder, *A.* 41, 317). Addition of NH_3Aq to a solution of AgSCy in NH_4SCy ppts. shining tablets of the *double compound* $AgSCy.NH_3$; loses all NH_3 by treatment with water (Gintl, *W. A. B.* 60, 474; Weith, *Z.* 1869. 310; *cf.* Gossmann, *A.* 100, 76). Solution of AgSCy in hot KSCyAq on cooling deposits the *double salt* AgSCy.KSCy; decomposed by water (Hull, *A.* 76, 93). The *double salt* $AgSCy.NH_4SCy$ is also known (Gossmann, *A.* 100, 76; Fleischer, *A.* 179, 225).

Sodium sulphocyanide NaSCy. H.F. [Na,S,Cy] = 77,100 (Joannis, *A. Ch.* [5] 26, 540). Prepared by neutralising HSCyAq by Na_2CO_3, evaporating, and crystallising from alcohol. Also by heating 1 pt. K_4FeCy_6 with 3½ pts. dry $Na_2S_2O_3$, and dissolving out with hot alcohol (Frohde, *P.* 119, 317; Meitzendorff, *P.* 56, 63). Very deliquescent rhombic plates; e. sol. alcohol. Forms the *double compound* $NaSCy.HgCy_2$ (Clève, *Bl.* [2] 23, 71).

Strontium sulphocyanide $Sr(SCy)_2.3H_2O$. Prepared by neutralising HSCyAq with $SrCO_3$, and evaporating at 100°, and then over H_2SO_4 (Meitzendorff, *P.* 56, 63). Gives off $3H_2O$ at 100°, and begins to decompose at 160°–170°. Forms the *double compound* $Sr(SCy)_2.2HgCy_2.4H_2O$ (Clève, *Bl.* [2] 23, 71).

Thallous sulphocyanide TlSCy. Small shining needles; by mixing Tl_2CO_3Aq with KSCyAq (Kuhlmann, *J. pr.* 88, 175; Hermes, *J. pr.* 97, 465). For crystalline form *v.* Miller (*Pr.* 14, 455). Forms a double salt with KSCy (Carstanjen, *J. pr.* 102, 129).

Tin sulphocyanide. The *stannous* salt $Sn(SCy)_2$ is obtained by heating freshly ppd. $SnO.xH_2O$ in HSCyAq, filtering, boiling, filtering again from SnO, and evaporating. Citron-yellow crystals; sol. water and alcohol; aqueous solution reflects blue light (Clasen, *J. pr.* 96, 349). Stannic hydrate scarcely dissolves in HSCyAq.

Uranium sulphocyanide $U(SCy)_2$. Dark green mass, by dissolving uranous hydrate in

HSCyAq and evaporating (Rammelsberg, *A.* 48, 235). Existence of uranic sulphocyanide is doubtful (*v.* Porret, *T.* 1814. 527).

Yttrium sulphocyanide $Y(SCy)_3.6H_2O$ (Clève a. Hoeglund, *Bl.* [2] 18, 197). Forms the *double compound* $Y(SCy)_3.3HgCy_2.12H_2O$ (Clève, *J. pr.* 91, 227).

Zinc sulphocyanide $Zn(SCy)_2$. White crystals; obtained by dissolving freshly ppd. $ZnCO_3$ in HSCyAq, evaporating, and crystallising from alcohol (Meitzendorff, *P.* 56, 63). Dissolves in NH_3Aq, rhombic prisms separate of the *double compound* $Zn(SCy)_2.2NH_3$; these are decomposed by water to ZnO and NH_4SCy (Meitzendorff, *l.c.*; Fleischer, *A.* 179, 225). Also forms the *double compounds* $Zn(SCy)_2.2HgCy_2.4H_2O$, and $Zn(SCy)_2.2HgCy_2.3NH_3$ (Clève, *Bl.* [2] 23, 71).

TELLUROCYANIDES. — A potassium tellurocyanide is probably momentarily formed when Te and KCy or K_4FeCy_6 are melted together, but if so it. is quickly decomposed on treatment with water with ppn. of Te (Berzelius, *S.* 31, 60). M. M. P. M.

CYANIDINE, a name proposed by Pinner (*B.* 18, 760) for derivatives of $C_3N_3H_3$ in which H_3 is displaced by hydrocarbon radicles, *e.g.* $C_3N_3Me'_3$ would be tri-methyl-cyanidine. These compounds are mostly described as paranitriles of the corresponding acids. See also CYANETHINE, CYANMETHETHINE, and CYANMETHINE.

CYANILIC ACID *v.* CYANIC ACIDS.

CYANINE or **QUINOLINE BLUE** *v.* QUINOLINE.

CYAN-METH-ETHINE $C_8H_{13}N_3$. [166°]. S. 2·7 at 20°.

Preparation.—Sodium (1 pt.) is added to a mixture of propionitrile (6·6 pts.) and acetonitrile (3·3 pts.). The sodium dissolves with evolution of gas. The product is freed from excess of nitriles by distillation, washed with water and fractionally crystallised from alcohol and benzene. Cyanethine is first obtained, but the chief portion is cyan-meth-ethine, formed thus: $2C_2H_5CN + CH_3CN = C_8H_{13}N_3$ (C. Riess a. E. v. Meyer, *J. pr.* [2] 31, 112).

Properties.—Trimetric plates (from benzene). Begins to sublime below 100°.

Salts.—$B',HCl,AuCl_3$. Plates.— $(B',HCl)_2PtCl_4$. Clustered needles.

Combination.—$B'_2,AgNO_3$.

Reactions.—1. *Bromine* warmed with a solution of the hydrobromide forms a colourless solution, out of which NH_3 throws down bromo-cyanmethethine, $C_8H_{12}BrN_3$. This is soluble in hot water, alcohol, ether, and benzene, and forms trimetric crystals [155°].—2. HCl at 180° forms an 'oxy-base' [150°].

CYANMETHINE $C_6H_9N_3$. [181°]. S. 156 at 18°. S. (alcohol) 19 at 18°.

Preparation.—From acetonitrile (methyl cyanide) (6 pts.) and sodium (1 pt.) (Baeyer, *B.* 2, 319; Keller, *J. pr.* [2] 31, 366). Marsh gas is evolved, not ethane.

Properties.—Very similar to cyanethine, but 2,140 times more soluble in water. It may be crystallised from alcohol. Its aqueous solutions give pps. with $AgNO_3$, $Pb(OAc)_2$, $HgCl_2$, and $BaCl_2$ (E. v. Meyer, *J. pr.* [2] 27, 152).

Combinations.—$(C_6H_9N_3)_2AgNO_3$. Rhombohedra (from hot water).

Reactions.—1. N_2O_3, passed into a solution of cyanmethine in glacial acetic acid, forms an oxy-base, $C_6H_7N_2(OH)$; the nitrate of this base, $C_6H_8N_2O,HNO_3$, separates as tufts of needles from the cold solution. The free base, $C_6H_8N_2O$, melts at [193°], and crystallises from alcohol in needles. This base is also formed by heating cyanmethine with HCl at 180° (Wollner, *J. pr.* [2] 29, 131). The nitrate of the oxy-base gives with $AgNO_3$, on neutralising with NH_3, a pp. of $C_6H_7AgN_2O$.—2. *Bromine* gives, even in the cold, a ***bromo-cyan-methine*** [142°]. Decomposed by boiling water, with formation of NH_4Br. Nitrous acid gas, passed into a solution of bromo-cyanmethine in glacial acetic acid, gives white needles of the nitrate of the **bromo-'oxy-base'**: $C_6H_7BrN_2O,HNO_3$ [158°]. This compound forms a silver derivative: $C_6H_6AgBrN_2O$. Bromo-cyan-methine retains its bromine much more strongly than bromo-cyanethine. It is converted by phenyl cyanate into a urea: $C_6H_6BrN_2.NH.CO.NPhH$ [186°-206°]. Bromine converts this into a tri-brominated urea, probably $C_6H_6BrN_2.NH.CO.NH.C_6H_3Br_2$ [257°]. 3. *Chlorine* forms a dichloride of chloro-cyanmethine, whence aqueous NH_3 liberates ***chloro-cyan-methine*** $C_6H_8ClN_3$. (Cyan-ethine forms a tri-chloro- derivative.) N_2O_3 converts the dichloride, $C_6H_8ClN_3Cl_2$, dissolved in glacial acetic acid, into the nitrate of the chloro-'oxy-base,' $C_6H_7ClN_2O,HNO_3$. [153°].—4. *Phenyl cyanate* (6 g.), warmed with cyanmethine (5 g.) dissolved in benzene, forms crystals of a complicated urea: $C_6H_7N_2.NH.CO.NPhH$. This melts at [225°]. Bromine added to its solution in HCl forms a di-bromo- derivative [238°].

Salts.—B'HCl: needles. — $B'_2H_2PtCl_6$. — B'HI. — $B'I_2$. — $B'HI_3$. — $B'HI_5$. — $B'HNO_3$. — $B'_2H_2SO_4$.—$B'(H_2SO_4)_2$.—$B'_2H_2C_2O_4$ 2aq.

Constitution. - The presence of amidogen in cyan-methine is shown by the action of phenyl cyanate and of N_2O_3 upon it. Other reactions indicate, however, that it is differently constituted to cyanethine.

CYANO-ACETIC ACID $C_3H_3NO_2$ *i.e.* $CN.CH_2.CO_2H$. *Semi-nitrile of malonic acid.* Mol. w. 85. [55°] (Van 't Hoff, *Ar. N.* 10, 274). Formed by boiling chloro-acetic ether (250 g.) with KCy (300 g.) and water (1,200 g.) (Hugo Müller, *A.* 131, 350; Meves, *A.* 143, 201).

Properties. — Crystalline; decomposed by heat into CO_2 and acetonitrile.

Reactions.—1. Boiling aqueous KOH gives malonic acid.—2. Br gives di-bromo-acetonitrile, bromoform, and CO_2 (Van 't Hoff, *B.* 7. 1383, 1571).—3. *Electrolysis* gives ethylene cyanide [38°] (Moore, *Am. S.* [3] 3, 177).

Salts.—KA': deliquescent. — ZnA'_2 2aq.— $HgA'_2$2HgO. – PbA'_2 aq.—MnA'_2 2aq (Engel, *Bl.* [2] 44, 424): beautiful crystals.—CuA'_2. —AgA'.

Ethyl ether EtA'. (207°).

Dissolves *sodium*, forming $CN.CHNa.CO_2Et$ as a white, very hygroscopic, and easily fusible powder. This sodium derivative is easily acted on by alkyl iodides, thus CH_3I gives rise to $CN.CH(CH_3).CO_2Et$ (194°). V.D. 4·34; C_2H_5I gives $CN.CH(C_2H_5).CO_2Et$ (204°). V.D. 4·63; C_3H_7I gives $CN.CH(C_3H_7).CO_2Et$ (215°-220°). ClCO.OEt acts easily upon the Na derivative, giving $CN.CH(CO_2Et)_2$. The mono-chlor- and mono-bromo-derivatives are formed with remarkable neatness. $CN.CHCl.CO_2Et$ is a colourless liquid, with a pungent odour (190°). V.D. 5·11 (Henry, *C. R.* 104, 1618; Haller, *Bl.* [2] 48, 27).

The following ethers have been obtained by the action of Na and ethyl or methyl cyanacetate upon the corresponding diazo-chlorides:—

Methyl benzene-azo-cyanacetate $C_6H_5.N_2.CH(CN).CO_2Me$. [86°].

Ethyl benzene-azo-cyanacetate $C_6H_5.N_2.CH(CN).CO_2Et$. [125°].

Methyl o-toluene-azo-cyanacetate $C_6H_4Me.N_2.CH(CN).CO_2Me$. [167°].

Methyl p-toluene-azo-cyanacetate $C_6H_4Me.N_2.CH(CN).CO_2Me$. [133°].

Ethyl o-toluene-azo-cyanacetate $C_6H_4Me.N_2.CH(CN).CO_2Et$. [126°].

Ethyl p-toluene-azo-cyanacetate $C_6H_4Me.N_2.CH(CN).CO_2Et$. [74°] (Haller, *C. R.* 106, 1171–1174).

Amide $CN.CH_2.CONH_2$. [118°]. Formed by dissolving cyano-acetic ether in aqueous ammonia, and allowing the solution to evaporate spontaneously. Crystallises from alcohol in small needles (Henry, *C. R.* 101, 1618).

Acetyl-cyano-acetic acid $CH_3.CO.CH(CN).CO_2H$.

Methyl ether MeA′. [47°]. From $CH_3.CO.CHNa.CO_2Me$ and cyanogen chloride in MeOH (Haller a. Held, *C. R.* 106, 210). Also from $CN.CHNa.CO_2Me$ and acetyl chloride.—$Ca(C_5H_4NO_3)_2$ 6aq: efflorescent crystals.

Ethyl ether EtA′. Formed similarly; *v.* CYANO-ACETO-ACETIC ETHER.

Propionyl-cyano-acetic ether $CH_3.CH_2.CO.CH(CN).CO_2Et$. (160°) at 50 mm. —$Ca(C_8H_{10}NO_3)_2$ 2aq.

***n*-Butyryl-cyano-acetic ether** $PrCO.CH(CN).CO_2Et$. (171°) at 66 mm. —CaA'_2 2aq.—BaA'_2 3½aq (Haller, *C. R.* 106, 1085).

Isobutyryl-cyano-acetic ether $iPr.CO.CH(CN).CO_2Et$. (173°) at 85 mm. — CaA'_2 2aq.

Benzoyl-cyano-acetic ether *v.* CYANO BENZOYL ACETIC ACID.

***o*-Toluyl-cyano-acetic ether** $C_6H_4Me.CO.CH(CN).CO_2Et$. [35°]. Prisms (Haller, *C. R.* 107, 104).— CaA'_2 4aq.

Phenyl-acetyl-cyano-acetic ether $CH_2Ph.CO.CH(CN).CO_2Et$. Oil.

Cinnamyl-cyano-acetic ether. [104°].

Di-cinnamyl-cyano-acetic ether $(PhCH:CH.CO)_2C(CN).CO_2Et$. Silky needles.

CYANO-ACETIC ALDEHYDE $CH_2(CN).CHO$. (72°). S.G. ^{15} ·881. V.D. 2·33. Formed by the action of AgCN as an alcoholic solution of iodo-acetic-aldehyde. Colourless mobile liquid. Miscible with most solvents. It does not solidify at −20°. It reduces Fehling's solution, forms a compound with $NaHSO_3$, and is resinified by NaHO and HCl. HNO_3 oxidises it to cyano-acetic acid. It forms with aniline a base [113°] (Chautard, *C. R.* 106, 1167–1169).

CYANO-ACETO-ACETIC ETHER $CH_3.CO.CH(CN).CO_2Et$. [27°]. (119°) at 20 mm. Formed by the action of potassium cyanide on chloro-aceto-acetic ether; the salt $CN.CH_2.C(OK):CH.CO_2Et$ being also formed in small quantity (James, *A.* 240, 61; *C. J.* 51, 287; *C. J. Proc.* 3, 25). Formed also by treating sodium aceto-acetic ether with cyanogen chloride, and from cyano-acetic ether and AcCl (Haller a. Held, *Bl.* [2] 47, 888; *C. R.* 95, 235; 104, 1627; 105, 115).

Properties.—Silky needles, cannot be distilled. Insol. water, sol. alcohol and ether. Gives a characteristic red colouration with Fe_2Cl_6. Decomposed by boiling alkalis into acetic acid, CO_2, and ammonia.

Salts. $NaC_7H_8NO_3$: crystals (from alcohol). KA′: needles (from alcohol); insol. ether and benzene.— CaA'_2 3aq: monoclinic crystals (from alcohol).

CYANO-ACETONE C_4H_5NO *i.e.* $CH_3.CO.CH_2CN$. (c. 123°). From chloro acetone and KCy in dilute alcohol (Matthews a. Hodgkinson, *B.* 15, 2679). Converted by alcohol and HCl into aceto-acetic ether.

Isomeride. [166°]. From chloro-acetone and aqueous KCN (Glutz, *J. pr.* [2] 1, 141; *cf.* Bender, *B.* 4, 518). Very volatile crystals. Forms a crystalline compound with HI.

ω-CYANO-ACETOPHENONE *v.* BENZOYL-ACETONITRILE.

***p*-Cyano-acetophenone** $[4:1]C_6H_4(CN).CO.CH_3$. [61°]. From *p*-amido-acetophenone by displacing NH_2 by Cy (Ahrens, *B.* 20, 2955). Needles (from dilute alcohol). Boiling alcoholic KOH converts it into acetophenone *p*-carboxylic acid (*q. v.*).

Oxim $C_6H_4(CN).C(NOH).CH_3$. [160°].

CYANO-ACETYL BROMIDE $CH_2(CN).COBr$. Appears to be formed, together with the isomeric bromo-acetyl cyanide, by heating AgCN with bromo-acetic acid and chloroform (Hubner, *A.* 124, 315; 131, 66). Needles (from ether or chloroform). Converted by KOH into cyano-acetic and malonic acids.

CYANO-ACETYL-DI-METHYL-UREA $NHMe.CO.NMe.CO.CH_2.CN$. [above 260°]. Prepared by the action of cyano-acetyl chloride on dimethylurea (Mulder, *B.* 12, 466).

CYANO-ACETYL-UREA $NH_2.CO.NH.CO.CH_2.CN$. [200°–210°]. Sl. sol. water and alcohol. Prepared by the action of cyano-acetyl chloride on urea (Mulder, *B.* 12, 465; *Bl.* [2] 29, 531).

CYANO-ANGELIC ETHER $C_3H_5.CH(CN).CO_2Et$. (c. 218°). From sodium cyano-acetic ether and allyl iodide (Henry, *C. R.* 104, 1618).

DI-CYANO-BENZENES *v.* *Nitriles of* *Iso*PHTHALIC and TEREPHTHALIC ACIDS.

***o*-CYANO-BENZOIC ACID** $C_8H_5NO_2$ *i.e.* $C_6H_4(CN).CO_2H$. *Semi-nitrile of phthalic acid.* Appears to be formed from *o*-amido-benzoic acid by the diazo-reaction, but changes spontaneously into the isomeric phthalimide (Sandmeyer, *B.* 18, 1499).

Ethyl ether A′Et: [70°]; needles; v. sol. alcohol, ether, &c., sl. sol. hot water. Obtained from anthranilic ether by diazotisation and treatment with $Cu_2(CN)_2$ (Muller, *B.* 19, 1498).

***m*-Cyano-benzoic acid** $C_6H_4(CN)CO_2H$ [1:3]. [217°].

Formation.—By the action of a hot solution of cuprous potassium cyanide upon *m*-diazo-benzoic chloride (Sandmeyer, *B.* 18, 1498).

Properties.—Microscopic needles. V. e. sol. ether, alcohol, and hot water. Gives isophthalic acid on saponification. By distillation of the Ca salt with lime benzonitrile is formed. By HNO_3 it is oxidised to isophthalic acid. By alcoholic H_2S

it is converted into the acid $C_{16}H_{10}O_4N_2S$ probably $C_6H_4(CO_2H).C(NH).S.C(NH).C_6H_4(CO_2H)$ [199°] whence tin and HCl give ω-imido-*m*-di-toluic acid. By treatment with fuming sulphuric acid and pouring the mixture into water it yields $C_{16}H_{10}O_5N_2$ probably $C_6H_4(CO_2H).C(NH).O.C(NH).C_6H_4(CO_2H)$. [above 300°].

Salts.—$C_6H_4(CN).CO_2Ag$: insoluble pp.—A'_2Ca 3aq : crystals, sol. hot water.—A'_2Ba $3\frac{1}{2}$aq : soluble crystals.—A'_2Zn : white pp.

Methyl ether A'Me : [65°]; crystals; v. sl. sol. water, v. sol. alcohol, ether, &c.

Ethyl ether A'Et : [56°]; crystals; nearly insol. water.

Amide $C_6H_4(CN).CONH_2$: [above 300°]; v. sol. alcohol and ether, insol. water.

Amidoxim $C_6H_4(CO_2H)C(NH_2):NOH$: [198°]; crystalline. Formed by the action of hydroxylamine upon *m*-cyano-benzoic acid (Bromme, *B.* 20, 524; *cf.* Muller, *B.* 19, 1494).

p-**Cyano-benzoic acid** $C_6H_4(CN)CO_2H$ [1:4]. Formed by the action of a hot aqueous solution of cuprous potassium cyanide upon *p*-diazo-benzoic chloride (Sandmeyer, *B.* 18, 1496). Quickly changes into terephthalamic acid.

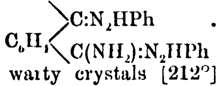
Ethyl ether A'Et : [54°], needles; v. sol. alcohol and ether (Muller, *B.* 18, 2485).

ISO-CYANO-BENZOPHENONE

$C_6H_5.CO.C_6H_4NC$. [119°]. From *p*-amido-benzophenone, chloroform, and alcoholic KOH (Dœbner, *B.* 14, 1838). Silky needles, when hot it smells unpleasant. HCl splits it up into formic acid and amido-acetophenone.

Di-*p*-cyano-benzophenone

$C_6H_4(CN).CO.C_6H_4(CN)$. [205°]. Formed by dry distillation of calcium *p*-cyano-benzoate. Warty crystals. Sublimable. V. sol. alcohol, ether, and benzene, slightly sol. petroleum-ether and hot water. With phenyl-hydrazine it yields the compound



$$\begin{array}{l} C_6H_4\diagup C(NH_2):N_2HPh \\ \qquad\quad\diagdown \\ \qquad\qquad C:N_2HPh \\ \qquad\quad\diagup \\ C_6H_4\diagdown C(NH_2):N_2HPh \end{array}$$

. The latter body forms warty crystals [212°]; v. sol. alcohol, ether, benzene, and CS_2 (Bromme, *B.* 20, 521).

Isocyano-benzophenone *v.* BENZOYL-PHENYL-CARBAMINE.

CYANO-BENZOYL-ACETIC ACID.

Methyl ether CBzHCy.CO_2Me. [74°]. From methyl cyano-acetate and BzCl (Barthe, *C. R.* 106, 1416). Long prisms, sol. ether and alcohol. Gives a red colour with $FeCl_3$. Its alcoholic solution has an acid reaction. Boiling water splits it up into CO_2 and Ph.CO.CH_2Cy [82°]. Its **sodium derivative** Cy.CBzNa.CO_2Me forms hard crystals, decomposing at 123°. Its **barium salt** Ba(CBzCy.CO_2Me)$_2$ aq is also crystalline.

Ethyl ether $C_{10}H_7NO_3$ *i.e.* $C_6H_5.CO.CH(CN).CO_2Et$. [41°]. From benzoyl-acetic ether, NaOEt, and CyCl. Also from CN.CHNa.CO_2Et, and BzCl (Haller, *C. R.* 101, 1270; 105, 130). Prisms; sol. alcohol, aqueous alkalis, and Na_2CO_3Aq. Gives an intense red colouration with Fe_2Cl_6. Boiling water forms cyano-acetophenone and CO_2. Alcoholic HCl gives CO_2 and acetic and benzoic ethers.

o-**CYANO-BENZYL-AMINE**

$C_6H_4(CN).CH_2.NH_2$. Formed, together with phthalic acid, by digesting phthal-*o*-cyano-benzyl-imide with fuming HCl. The solution of its hydrochloride is converted by nitrous acid into nitroso-phthalimidine. B'HCl aq : glistening needles. **Picrate** $B'C_6H_2(NO_2)_3OH$: sparingly soluble yellow crystalline pp. (Gabriel, *B.* 20, 2232).

o-**CYANO-BENZYL CHLORIDE**

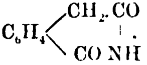
$C_6H_4(CN).CH_2Cl$ [1:2]. [61°]. (252° at 758 mm.). Monosymmetrical colourless crystals *a*:*b*:*c* = ·7775 : 1 : ·2939, β = 60° 2′. Prepared by leading chlorine into nearly boiling *o*-cyano-toluene till its weight has increased by 30 p.c. (Gabriel a. Otto, *B.* 20, 2222).

o-**CYANO-BENZYL-CYANIDE**

$C_6H_4(CN).CH_2.CN$ [1:2]. *o-Cyano-phenyl-acetonitrile.* [81°].

Preparation.—*o*-Cyano-benzyl chloride (30 pts.) is added to a solution of 15 pts. of potassium cyanide (96–98 p.c. KCN) in 60 c.c. of water and 300 c.c. of alcohol. After cohobating for $\frac{3}{4}$ hour, $\frac{2}{3}$ of the alcohol is distilled off and the residue poured into water (about $\frac{1}{2}$ litre); the crystals which separate are recrystallised from alcohol (yield : 25 pts.) (Gabriel a. Otto, *B.* 20, 2224, 2502).

Properties.—Colourless plates. V. sol. ordinary solvents. By warming with alcoholic sodium ethylate and MeI or EtI it is converted into $C_6H_4(CN).CHMe.CN$ or $C_6H_4(CN).CHEt.CN$. By heating with conc. H_2SO_4 at 80°, and pouring the product into water it is converted into the imide of phenyl-acetic-*o*-carboxylic acid



$$C_6H_4\left\langle\begin{array}{l}CH_2.CO\\ \qquad\;\;|\\ CO\,NH\end{array}\right.$$

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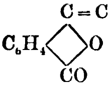
ω-CYANO-BENZYLIDENE-PHTHALIDE

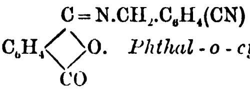


$$C_6H_4\left\langle\begin{array}{c}C{=}C(CN).C_6H_5\\ \diagdown\;\;\diagup\\ O\\ \diagup\;\;\diagdown\\ CO\end{array}\right\rangle$$

[165°]. Fine yellowish needles. Formed by heating phthalic anhydride with benzyl cyanide, best with addition of dry sodium acetate (Gabriel, *B.* 18, 1264).

o-**CYANO-BENZYL-PHTHALIMIDE**

$C_{16}H_{10}N_2O_2$ *i.e.*



$$C_6H_4\left\langle\begin{array}{c}C{=}N.CH_2.C_6H_4(CN)\\ \diagdown\;\;\diagup\\ O\\ \diagup\;\;\diagdown\\ CO\end{array}\right\rangle$$

. *Phthal-o-cyano-benzyl-imide.* [182°]. Prepared by heating phthalimide-potassium (9 pts.) with *o*-cyano-benzyl chloride (7 pts.) slowly from 100° to 120°. Large prisms. By boiling with fuming HCl it is split up into phthalic acid and *o*-cyano-benzyl-amine (Gabriel, *B.* 20, 2231).

exo-**CYANO-BENZYL-UREA** *v.* PHENYL-URAMIDO-ACETONITRILE.

CYANO-BORNEOL. Has been shown by Haller to be bornyl carbamate (*q.v.*). *V.* also CINEOL.

p-**CYANO-ISOBUTYL-BENZENE** *v.* *Nitrile of p-(iso)*-BUTYL-BENZOIC ACID.

α-**CYANO-BUTYRIC ACID**

$CH_3.CH_2.CH(CN).CO_2H$.

Ethyl ether EtA'. (209° cor.). S.G. º 1·009. From α-bromo-butyric ether, alcohol, and $HgCy_2K_2Cy_2$ at 130° (Markownikoff, *A.* 182, 330). Also from sodium cyano-acetic ether and EtI (Henry, *C. R.* 101, 1618).

Amide $CH_3.CH_2.CH(CN).CONH_2$. [113°]. Pearly scales (from alcohol).

CYANO-BUTYRO-ACETIC ETHER $CH_2Me.CH_2.CO.CHCy.CO_2Et$. (c. 172°) under 66 mm. From sodium cyano-acetic ether and butyryl chloride (Haller, *C. R.* 106, 1083).—CaA'_2 2aq.—BaA'_2 3aq.

Cyano-iso-butyro-acetic ether $CHMe_2CO.CHCyCO_2Et$. (174°) at 85 mm. Formed as above from isobutyryl chloride (H.).—$CaA'_2$2aq.

CYANO-CAMPHOR *v.* Camphor.

CYANO-CARBIMIDAMIDO-BENZOIC ACID *v.* vol. i. p. 157.

CYANO-CARBONIC ACID *v.* Cyanoformic acid.

CYANO-CARBOXAMIDO-BENZOIC ACID *v.* vol. i. p 157.

CYANO-TRI-CARBALLYLIC ETHER $C_{13}H_{19}NO_6$ *i.e.* $C(CN)(CO_2Et)(CH_2CO_2Et)_2$. [41°]. (187°). Formed in small quantities in the preparation of cyano-succinic ether (*q. v.*). It is also formed from cyano-succinic ether by Na and chloro-acetic ether. Colourless. Sol. alcohol and ether; insol. water and alkalis (Haller a. Barthe, *C. R.* 106, 1414).

ω-CYANO-CINNAMYL-UREA *v.* *Nitrile of* Phenyl-α-uramido-crotonic acid.

CYANO-CROTONIC ACID $C_4H_4(CN)O_2H$. When liberated from its salts by an acid, it changes to acid ammonic crotaconate.

Salt.—KA′. From α-chloro-crotonic acid, cold dilute alcohol and KCy (Claus a. v. Wasowicz, *A.* 191, 69). Boiled with KOH it forms crotaconic acid (*q. v.*).—AgA′.

β-Cyano-crotonic ether $CH_3.C(CN):CH.CO_2Et$. [71°]. From aceto-acetic ether, formamidine hydrochloride, and dilute aqueous Na_2CO_3 (Pinner, *B.* 18, 2846). Needles (from ether).

CYANO-ETHYL-ACETO-ACETIC ETHER $CH_3.CO.C(CN)Et.CO_2Et$. (108°) at 18 mm. S.G. ^{20} ·976. From sodium aceto-acetic ether and CyCl, followed by water (Held, *C. R.* 98, 522). Oil; insol. aqueous alkalis. Boiling aqueous KOH gives acetic and butyric acids, NH_3, and CO_2.

CYANOFORM $CHCy_3$. From chloroform and alcoholic KCy at 130° (Fairley, *C. J.* 11, 362; Pfankuch, *J. pr.* [2] 4, 38; 6, 97. According to Claus, *A.* 191, 35, cyanoform does not exist). Small needles. Decomposed by HCl into NH_3 and methane tricarboxylic acid $CH(CO_2H)_3$.

Compound.—With *mercuric iodide*: $3HgI_2,(CHCy_3)_2$, crystalline needles got by heating iodoform with alcoholic $HgCy_2$ at 120°.

CYANO-FORMIC ACID $CN.CO_2H$. *Cyano-carbonic acid. Semi-nitrile of oxalic acid.*

Methyl ether $CN.CO_2Me$. (101°). From methyl oxamate $NH_2.CO.CO_2Me$ and P_2O_5 (Weddige, *J. pr.* [2] 6, 117; 10, 193). Pungent oil. Quickly decomposed by water into HCy, methyl alcohol, and CO_2. Combines with H_2S, forming $NH_2.CS.CO_2Me$.

Ethyl ether $CN.CO_2Et$. (116°). Formed by distilling oxamic ether with P_2O_5. Formed also by distilling $NH_2.CCl_2.CO_2Et$, the product of the action of PCl_5 on oxamic ether (Wallach, *A.* 184, 12; *B.* 8, 299). Oil, lighter than water. Slowly decomposed by cold water into CO_2, alcohol, and HCy. Conc. HCl gives oxalic acid. Ammonia forms NH_4Cy and carbamic ether; alkylamines act similarly. HI reduces it to amido-acetic ether.

Isobutyl ether $CN.CO_2CH_2Pr$. (146°).

Allyl ether $CN.CO_2C_3H_5$. (135°). From di-cyano-propyl alcohol (dicyanide of allyl alcohol) and fuming HCl (Wagner a. Tollens, *B.* 5, 1045).

Amide $CN.CONH_2$. [60°]. Formed, together with oxamide, by passing cyanogen into 96 p.c. acetic acid and, after a few hours, heating to 100° (Beketoff, *J. R.* 7, 99). Tables, v. sol. water, alcohol, and ether. Split up at 120° into HCy and cyanuric acid.

Di-ethyl amide $CN.CO.NEt_2$. (220°) From *u*-di-ethyl-oxamide and P_2O_5 (Wallach, *B.* 14, 737). Oil; volatile with steam; sl. sol. water. Lighter than water. PCl_5 gives 'chlor-oxalethyline.'

Para-**cyano-formic acid** $(CN.CO_2H)_n$. From its ethers by treatment with cold aqueous KOH; the acid is then ppd. by HCl as a bulky mass, insol. alcohol and ether, v. sl. sol. water. Boiling water converts it into oxalic acid and NH_3.

Salts.—$K_n(C_2NO_2)_n$: long needles (from water).—$Ag_n(C_2NO_2)_n$: yellow pp., insol. HNO_3.

Methyl ether $Me_n(COCN)_n$. [154°]. Obtained by polymerisation from methyl cyanoformate under the influence of HCl. Also from the silver salt and MeI. Small needles.

Ethyl ether $Et_n(COCN)_n$. [165°]. Formed by saturating cyano-formic ether with HCl and heating the liquid to 100° for several hours, or leaving it to itself in the cold for a few weeks (Weddige). Six-sided prisms, v. sl. sol. cold, sl. sol. hot, alcohol. Cannot be distilled. Boiling alkalis give oxalic acid, NH_3, and alcohol.

Isobutyl ether $(PrCH_2)_n(COCN)_n$. [158°].

Amide $(CN.CO.NH_2)_n$. Amorphous.

Methylamide $(CN.CO.NHMe)_n$. [250°]. Needles.

Anilide $(CN.CO.NHPh)_n$. Needles.

CYANOGEN CN. Mol. formula C_2N_2. Mol. w. 52·96. [−34·4°] (Faraday, *A.* 56, 158; Loir a. Drion, *J.* 1860. 41). (c. −20°) (Bunsen, *P.* 46, 101). S.G. ·866 at 17° (Faraday). V.D. 1·805. S. (gas) at 20° = 4½; S. (gas) in alcohol at 20° = 23; S. (gas) in ether at 20° = 5. Vapour-pressure in atmos. at −17·7° = 1·25, at −9·4° = 1·72, at −5° = 2, at 0° = 2·37, at +6·9° = 3, at 17·2° = 4, at 25° = 5, at 31·3° = 6, at 37·4° = 7 (Faraday, *l.c.*), μ_D = 1·000804, μ_E = 1·000834, μ_G = 1·000895 (Croullebois, *A. Ch.* [4] 20, 185; *v.* also Chappuis a. Rivière, *C. R.* 103, 37). H.F. $[C^2,N^2] = -65,700$; H.C. $[C^2N^2,O^4] = 259,620$ (*Th.* 2, 388). For spectrum *v.* Wüllner (*P.* 144, 517), and Ciamician (*W. A. B.* 79 [2nd part], 8); dispersion *v.* Croullebois (*A. Ch.* [4] 20, 185), and Mascart (*C. R.* 71, 617, 679). For transpiration-coefficient *v.* Meyer (*P.* 143, 14).

Cyanogen was first prepared by Gay-Lussac in 1815; he compared cyanogen with chlorine, and the compounds of one with those of the other, hence arose the conception of the *compound radicle* CN replacing the *simple radicle* Cl. The name cyanogen (from *κύανος*) was suggested by the colour of Prussian blue, which was the earliest known compound of cyanogen.

The formula Cy is often used to denote cyanogen.

Occurrence.—In the gas from coke-ovens (Bunsen a. Playfair, *J. pr.* 42, 145).

Formation.—1. By passing induction-sparks between carbon poles in an atmosphere of N

(Morren, *C. R.* 48, 342). — 2. By heating $(NH_4)_2C_2O_4$ or $C_2O_2(NH_2)_2$, either alone or with dehydrating agents (Dumas, *A.* 10, 295; Bertagnini, *A.* 104, 176).—3. By heating AgCN (Delbrück, *A.* 64, 296) or $Au(CN)_3$ (Himly, *A.* 42, 157, 337).

Preparation.—Perfectly *dry* mercuric cyanide is heated in a dry flask or small retort with a long exit tube dipping under mercury in an inverted tube; the cyanide is decomposed to cyanogen and mercury, which condenses in the exit tube.

Properties.—A colourless gas, with penetrating odour resembling that of HCN. Very poisonous. Burns with purple flame. Liquefied by cold and pressure; at −20·7° at ordinary pressure; liquefaction may be effected by heating $Hg(CN)_2$ or porous charcoal saturated with cyanogen (Melsens, *C. R.* 77, 781) in a Faraday-tube (*cf.* also Hofmann, *B.* 3, 663). At very low temperatures freezes to a crystalline, ice-like mass. Liquid cyanogen is a colourless, mobile liquid; non-conductor of electricity; dissolves P, I, camphor, and various other bodies (*v.* Gore, *C. N.* 21, 303). Cyanogen gas is absorbed by Hg at c. 100° (Amagat, *C. R.* 68, 1170); it is also largely absorbed by porous charcoal (Hunter, *C. J.* [2] 9, 76; 10, 642). Cyanogen combines with several non-metals, *e.g.* with Cl, Br, I, S, P; it also forms compounds with most of the metals; in its chemical relations it shows analogies with the halogens, *e.g.* in the composition and properties of the acids HM and HMO, where M = Cl, Br, or CN, and in the composition of many cyanides. The hydracid HCN is much weaker than the corresponding halogen acids. Substitution of H in aromatic hydrocarbons by the group CN generally results in the production of compounds one or more H atoms in which are acidic (*v.* Meyer, *B.* 20, 2944; Schneidewind, *B.* 21, 1323; Papcke, *B.* 21, 1331; Knoevenagel, *B.* 21, 1314). The modes of preparation of cyanogen, *e.g.* from $(NH_4)_2C_2O_4$, and its reaction with H_2O to form $C_2O_2(NH_2)_2$, show that it is the nitrile of oxalic acid.

Reactions.—1. *Heated* to c. 500° paracyanogen is slowly formed (Troost a. Hautefeuille, *C. R.* 66, 735, 795; *v.* also PARACYANOGEN), at c. 1200° N is liberated (Meyer a. Goldschmidt, *B.* 15, 1161). Heated in presence of iron or platinum C and N are formed.—2. Decomposed to C and N by a series of *electric sparks*, but after a time re-formation of Cy begins (Buff a. Hofmann, *A.* 113, 129; Andrews a. Tait, *Pr.* 10, 427).—3. *Water* dissolves Cy, the solution slowly decomposes, except an acid be present (Gianelli, *J.* 1856. 435), with separation of brown flocks of azulmic acid (Pelouze a. Richardson, *A.* 26, 63), and formation of NH_4 oxalate and carbonate (Vauquelin, *A. Ch.* 9, 113; 22, 132), and also HCN and $CO.2NH_2$ (Wöhler, *P.* 15, 627).—4. *Alcoholic* and *ethereal solutions* decompose similarly to aqueous solutions (Buff a. Hofmann, *A.* 113, 129; Marchand, *J. pr.* 18, 104).—5. *Water in presence of aldehyde* produces oxamide.—6. With *sulphuretted hydrogen* either *cyan-thio-formamide* ($CN.CS.NH_2$) (*q. v.*) or *dithio-oxamide* ($NH_2.CS.CS.NH_2$) (*q. v.*) is formed, according as the Cy or the H_2S is in excess.—7. *Chlorine* reacts only in presence of moisture and sunlight, CNCl and $(CN)_3Cl_3$ are formed (Serullas, *A. Ch.* [2] 35, 291, 337).—8. *Hydrogen* at 500°-550° forms HCN (Berthelot, *Bl.* [2] 33, 2); HCN is also produced when electric sparks are passed through a mixture of Cy and H (Boillot, *C. R.* 76, 1132). *Nascent hydrogen* (Zn and HClAq) produces *ethylene-diamine* (*q. v.*) (Fairley, *A. Suppl.* 3, 371).—9. *Potassium* and *sodium* heated in Cy form cyanides.—10. Strongly heated *iron* decomposes Cy with formation of C and N.—11. *Zinc* forms cyanide, rapidly at 100°; *cadmium, copper,* and *lead*, at high temperatures, form small quantities of cyanides; *mercury* and *silver* do not react (Berthelot, *Bl.* [2] 33, 2).—12. When a mixture of Cy and *oxygen* is submitted to a powerful electric spark, explosion occurs with production of CO and CO_2; with a weak spark no explosion occurs; the explosion is not dependent on the dryness of the gases; slow combustion occurs in presence of strongly heated Pt (Dixon, *C. J.* 49, 384).—13. Conc. cold *hydrochloric acid* produces oxamide (Schmidt a. Glutz, *B.* 1, 66); HCl in absolute alcohol forms oxalic ether (Volhard, *A.* 158, 118; Pinner a. Klein, *B.* 11, 1481).—14. Conc. *hydriodic acid* when cold forms oxamide (Schmidt a. Glutz, *B.* 1, 66); when hot forms glycocoll (Emmerling, *B.* 6, 1352); at 280° forms NH_3 and C_2H_4 (Berthelot, *J.* 1867. 347).—15. With *potash*, cyanide and cyanate are formed.—16. With *dry ammonia*, *hydrazulmin*, $C_4H_6N_6$ (*q. v.* vol. i. p. 429), is formed; when Cy is passed into very conc. NH_3Aq, *azulmic acid*, $C_4H_5N_5O$ (*q. v.* vol. i. p. 429), is produced; with dilute NH_3Aq oxamide is formed along with NH_4, oxalate, and oxamate.

Combinations.—1. With *hydrogen* to form HCN (*v. Reactions*, No. 8).—2. With *water* in presence of aldehyde to form oxamide.—3. With *sulphuretted hydrogen* to form cyan-thio-formamide or dithio-oxamide (*v. Reactions*, No. 6).—4. With *ammonia* to form hydrazulmin, &c. (*v. Reactions*, No. 16).—5. With some *metals* to form cyanides (*v. Reactions*, Nos. 9, 10, 11).

POLYMERIDE OF CYANOGEN. **Paracyanogen** xCN. When $HgCy_2$ or AgCy is heated, a part is changed to a loose, brownish-black solid, having the composition xCN; the value of x is unknown; Maumené thinks it may be 4 (*Bl.* 35, 597). Liquid cyanogen is slowly polymerised by heating (at 350°-500°, Troost a. Hautefeuille, *C. R.* 66, 735, 795). Paracyanogen is prepared by heating dry $HgCy_2$ to 440° in a closed tube for 24 hours, and then passing cyanogen into the tube at the same temperature to volatilise and remove the Hg (T. a. H., *l.c.*). The quantity of paracyanogen formed depends on the temperature and pressure. Heated to 800° in a closed tube, or heated in a stream of CO_2 or N, paracyanogen is changed to cyanogen. At each temperature equilibrium results between the cyanogen and paracyanogen when a definite pressure is attained; T. a. H. give the following data:—

Temp.	Equilibrium-pressure
502°	34 mm.
506	56 „
559	123 „
575	129 „
587	157 „
599	275 „
601	318 „
629	868 „
640	1310 „

Heated in H paracyanogen forms HCN, NH_3, and C (Delbruck, *J. pr.* 41, 161). With molten KOH it forms KCN and KCNO; boiled with conc. KOHAq it is slowly dissolved with evolution of NH_3; by prolonged boiling with conc. HNO_3Aq it forms a yellow solution.

Cyanogen bromides. Two are known, CNBr and *x*CNBr, *x* probably = 3. Mol. w. of the polymeride is not known with certainty, analogy with $C_3N_3Cl_3$ points to formula $C_3N_3Br_3$. For preparation, &c., *v.* Cyanogen bromide and Cyanuric bromide, under Cyanic acid, p. 313.

Cyanogen chlorides. Two are known, CNCl and $C_3N_3Cl_3$ *v.* under Cyanic acid, p. 312.

Cyanogen iodides. Two are known, CNI and a polymeride which is probably $(CN)_3I_3$; *v.* under Cyanic acid, p. 313.

Cyanogen phosphide $(CN)_3P$. (*Phosphorus cyanide.*) Mol. w. not determined. White needles; very easily decomposed in contact with moist air to P, H_3PO_3, and HCN. Melts at 200°–203°, and boils a few degrees higher. Takes fire when slightly heated in air. Sl. sol. ether, CS_2, and PCl_3. With alcohol forms ethylic phosphite and HCN. Prepared by moistening AgCy with PCl_3 at a low temperature, closing the tube, and heating to 130°-140° for 6 hours, warming (after opening the tube) to remove excess of PCl_3, and heating residue to 130°–140° in a stream of dry CO_2 till the $P(CN)_3$ sublimes (Hubner a. Wehrhane, *A.* 127, 251; 132, 277).

Cyanogen selenide ?$(CN)_2Se$ (Schneider, *P.* 129, 634). Colourless plates; obtained in small quantity by adding dry AgCy to a solution of Se_2Br_2 in CS_2, and crystallising from CS_2. Decomposed by hot water to Se, H_2SeO_3, and HCN.

Cyanogen sulphides $(CN)_2S$, and $(CN)_2S_3$. Mol. w. of neither has been determined.

I. Cyanogen sulphide. (*Sulphur cyanide. Sulphocyanic anhydride.*) $(CN)_2S$. Produced by reaction between SI_2 and AgCy, SCl_2 and $HgCy_2$, and CyI and Ag_2S. Prepared by mixing ethereal solution of CyI with an equivalent quantity of AgNCS, evaporating with constant stirring, and allowing to stand in a small closed vessel; the residue is treated with boiling CS_2 which dissolves the Cy_2S, leaving AgI; the liquid is cooled to 0°, and the crystals are dried *in vacuo* over H_2SO_4. Forms rhombic plates melting at c. 60°; decomposed by heating in moist air; sol. ether, alcohol, and water; decomposed by H_2SO_4Aq, HClAq, or HNO_3Aq; with NH_3 forms NH_4CyS; with H_2S forms HCN, HCNS, and S (Linnemann, *A.* 120, 36).

II. Cyanogen persulphide $(CN)_2S_3$. Obtained along with $(CN)_2S$ in reaction between AgCy and SCl_2. Exists in two forms: (1) colourless crystalline mass, sol. CS_2; (2) dark-yellow powder, formed by spontaneous change of (1), insol. alcohol, ether, water, or CS_2, becomes electrical when rubbed (Schneider, *J. pr.* [2] 32, 187).

III. The compound $C_3N_3HS_3$ is sometimes called Pseudocyanogen sulphide. This body is produced by the action of oxidisers on HSCN or on soluble sulphocyanides. Obtained by passing Cl into KSCNAq, or gently warming a solution of 1 pt. KSCN in 3 pts. water with ½ its weight of conc. HNO_3Aq; the yellow pp. is repeatedly washed with hot water ($H_2C_2N_2S_3$ is dissolved out, Jamieson, *A.* 59, 339), then with CS_2 (which removes S, Linnemann, *A.* 120, 36), it is then dissolved in conc. H_2SO_4, re-ppd. by water, dried, boiled with absolute alcohol and again dried (Volckel, *A.* 89, 126; Letmi, *B.* 8, 767; Laurent a. Gerhardt, *A. Ch.* [3] 19, 98; Liebig, *P.* 15, 546; Wohler, *G. A.* 69, 271). Insol. in water, alcohol, and ether; sol. without change in conc. H_2SO_4 and in dilute alkalis; sl. sol. in NH_3Aq. Decomposed by molten KOH to KSCy and KCyO; heated with conc. NH_3Aq to 100° NH_4SCy and $C_3H_5N_5S$ (thio-ammelin) are formed. Heated with PCl_5 reacts thus $C_3S_3N_3H + 3PCl_5 = C_3N_3Cl_3 + 2PCl_3 + PSCl_3 + S_2Cl_2 + HCl$ (Ponomareff, *C. R.* 79, 1335). Heated alone, gives CS_2, S, and mellone ($C_6N_9H_3$) (Liebig, *P.* 15, 546). Heated with Cl, forms CyCl, S_2Cl_2, and mellone. Conc. HClAq at 130°–140° produces CS_2, S, and cyanuric acid. Not acted on by nascent H, nor by HIAq (Glutz, *A.* 154, 39, 44, 48).

M. M. P. M.

CYANOGEN HYDROXIDE *v.* Cyanic acid.

CYANO-MALONIC ETHER $CN.CH.(CO_2Et)_2$. Formed by acting on sodium malonate with cyanogen chloride. Formed also from sodium cyano-acetic ether and $ClCO_2Et$ (Haller, *Bl.* [2] 39, 262; *C. R.* 95, 143; 105, 169). Strong acid, forming crystalline lead and calcium salts. Boiling alkalis give malonic acid.

Salts.—$NaCCy(CO_2Et)_2$: slender needles.—CaA'_2 2½aq: triclinic prisms.—PbA'_2 aq. [88°]. Needles.

CYANO-MELAMIDINE *v.* Guanidine.

CYANO-METHYL-ACETO-ACETIC ETHER $CH_3.CO.CMe(CN).CO_2Et$. (c. 93°) at 20 mm. S.G. $\frac{20}{20}$ ·996. From methyl-aceto-acetic ether, NaOEt, and CyCl (Held, *C. R.* 98, 522; *Bl.* [2] 41, 330). Oil; insol. alkalis. Boiling alkalis form acetic and butyric acids.

CYANO-NAPHTHALENE *v. Nitrile of* Naphthoic acid.

CYANO-NAPHTHOPHENAZINE $C_{16}H_9CyN_2$ [237°]. From sodium naphthophenazine sulphonate by distilling with KCy and K_4FeCy_6 (Brunner a. Witt, *B.* 20, 2660). Alcoholic KOH gives naphthophenazine carboxylic acid [above 360°].

α-CYANO-(α)-NAPHTHYL-α-AMIDO-PROPIONIC ACID $CH_3.C(CN)(NHC_{10}H_7).CO_2H$.

Ethyl ether A'Et. [134°]. Formed by digesting α-cyano-α-oxy-propionic ether with (α)-naphthylamine. Small white plates; sol. hot water, sparingly cold, v. sol. alcohol and benzene (Gerson, *B.* 19, 2968).

α-Cyano-(β)-naphthyl-α-amido-propionic acid $CH_3.C(CN)(NHC_{10}H_7).CO_2H$.

Ethyl ether A'Et. Formed by heating α-cyano-α-oxy-propionic ether with (β)-naphthylamine. Small rosettes; sol. benzene and hot alcohol, nearly insol. water and cold alcohol (Gerson, *B.* 19, 2969).

α-CYANO-α-OXY-PROPIONIC ACID $CH_3.C(OH)(CN).CO_2H$. *Pyruvic-acid-cyanhydrin.* Crystals (containing EtOH); [151°]. Formed by slowly adding pyruvic acid to KCN suspended in boiling alcohol (Gerson, *B.* 19, 2963).

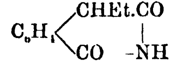
CYANO-PHENOL *v. Nitrile of* Oxy-benzoic acid.

o-CYANO-PHENYL-ACETO-NITRILE *v.* o-Cyano-benzyl cyanide.

β-CYANO-PHENYL-β-AMIDO-BUTYRIC ETHER $CH_3.C(CN)(NHPh).CH_2.CO_2Et$. Formed by the action of aniline upon the cyanhydrin of acetoacetic ether (Schiller-Wechsler, *B.* 18, 1039).

α-**CYANO-*α*-PHENYL-AMIDO-PROPIONIC ETHER** $CH_3.C(CN)(NHPh).CO_2Et$. [102°]. Formed by digesting an alcoholic solution of *α*-cyano-*α*-oxy-propionic ether with aniline for 24 hrs. at 80°. Large trimetric crystals, *a*:*b*:*c* = ·7902:1·0:1·56366 (Gerson, *B.* 19, 2963).

o-**CYANO-PHENYL-BUTYRONITRILE** $C_6H_4(CN).CHEt.CN$. *α-Ethyl-homo-o-phthalo-nitrile.* [40°]. (294°). Formed by warming *o*-cyano-benzyl-cyanide $C_6H_4(CN).CH_2.CN$ with alcoholic NaOEt and EtI. Short thick prisms. By heating with conc. H_2SO_4 and pouring into water it is converted into the imide of phenyl-ethyl-acetic-*o*-carboxylic acid



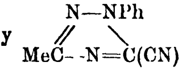
$$C_6H_4\begin{cases}CHEt.CO \\ \quad\quad | \\ CO\ -NH\end{cases}$$

(Gabriel, *B.* 20, 2505).

DI-CYANO-DI-PHENYL-ETHANE CN.CHPh.CHPh.CN. [218°]. Crystalline solid. *Formation.*—1. By reduction of di-cyano-di-phenyl-ethylene with sodium-amalgam.—2. Together with di-cyano-di-phenyl-ethylene by boiling phenyl-bromo-acetonitrile with an excess of alcoholic KCN (Reimer, *B.* 14, 1799).

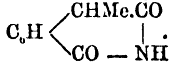
DI-CYANO-DI-PHENYL-ETHYLENE CN.CPh:CPh.CN. *Di-cyano-stilbene* [158°]. Colourless plates. Insol. water, sol. hot alcohol, benzene, acetic acid, and CS_2. Prepared by the action of bromine on benzyl cyanide, or from phenyl-bromo-acetonitrile by heating to 170°, or, better, by boiling with alcoholic KCN (Reimer, *B.* 13, 742; 14, 1798). By boiling with alcoholic KOH it gives diphenyl-fumaric anhydride. By reduction with zinc and HCl it gives a compound of the constitution $C_{16}H_{14}N_2$ which forms small needles melting at [208°]; insol. water, sol. alcohol.

CYANO-PHENYL-METHYL-TRIAZOLE $C_{10}H_8N_4$ probably



[109°]. Formed by the action of acetic anhydride upon di-cyan-phenyl-hydrazine. Also by warming di-cyan-phenyl-hydrazine with pyruvic acid in alcohol: $Ph.N(NH_2).C(CN):NH + CH_3.CO.CO_2H = C_{10}H_8N_4 + HCO_2H + H_2O$. By alcoholic KOH it is converted into phenyl-methyl-triazole-carboxylic acid [170°] (Bladen, *B.* 19, 2598).

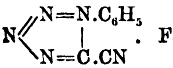
o-**CYANO-PHENYL-PROPIO-NITRILE** $C_6H_4(CN).CHMe.CN$. *α-Methyl-homo-o-phthalo-nitrile.* [37°]. (285°). Large trimetric crystals; *a*:*b*:*c* = ·9149:1:1·0809; *α* = 97°2′, *β* = 103°13′, *γ* = 87° 11′. Prepared by warming an alcoholic solution of *o*-cyano-benzyl-cyanide (*o*-cyano-phenyl-aceto-nitrile) with KOH and methyl iodide. V. sol. ordinary solvents, sl. sol. ligroin. By heating with conc. H_2SO_4 at c. 130° and pouring into water it yields the imide of phenyl-methyl-acetic-carboxylic acid



$$C_6H\begin{cases}CHMe.CO \\ \quad\quad\ | \\ CO - NH\end{cases}.$$

(Gabriel, *B.* 20, 2503).

CYANO-PHENYL-TETRAZOLE



$$N\begin{cases}N{=}N.C_6H_5 \\ \quad\ \ | \\ N{=}C.CN\end{cases}$$

. Formed by the action of nitrous acid upon di-cyano-phenyl-hydrazine. On saponification it gives phenyl-tetrazole-carboxylic acid (Bladin, *B.* 18, 2907).

α-**CYANO-PROPIONIC ACID** $CH_3.CH(CN).CO_2H$.

Ethyl ether EtA′. (194°). V.D. 4·34. From sodium cyano-acetic ether and CyCl (Henry, *C. R.* 101, 1618). Heavy oil.

β-**Cyano-propionic acid.** *Amide* $CN.CH_2.CH_2.CONH_2$. Formed, together with ethylene cyanide, by digesting ethylene bromide with alcoholic KCy (Pinner, *B.* 16, 360). Prisms (from water).

Cyano-propionic acid (?) $C_4H_5NO_2$. Prepared by dissolving wool (1 pt.) in water by means of KOH (3 pts.), and oxidising by $KMnO_4$ (2 pts.) (Wanklyn a. Cooper, *P. M.* [5] 7, 356). Amorphous, pale yellow, brittle solid (containing 1½ aq). Softens at 100°. V. sol. water and alcohol. When strongly heated it gives off acetonitrile. Potash-fusion gives ethylamine and oxalic acid.

Salts.—Sol. water, but not in alcohol.—KA′aq.—KA′4aq.—KA′5aq.—$CaA'_2$4aq (at 100°).—$BaA'_2$3aq (at 100°).—$Ba_4A'_4O$ 7aq.—PbA'_2aq (at 100°).—$MgA'_2$3aq.—AgA′¼aq (at 100°).—$Ag_4A'_2(OH)$ aq (at 100°).

CYANO-PROPIONYL-ACETIC ETHER $CH_2Me.CO.CHCy.CO_2Et$. (160°) at 50 mm. From sodium cyano-acetic ether and propionyl chloride (Haller, *C. R.* 106, 1083).—$CaA'_2$2aq: long needles, v. sol. water.

DI-CYANO-PROPYL ALCOHOL $CH_2Cy.CHCy.CH_2OH$. (151°). From allyl alcohol and cyanogen (Tollens, *B.* 5, 621).

CYANO-PYRIDINE *v. Nitrile of* PYRIDINE CARBOXYLIC ACID.

CYANO-QUINOLINE *v. Nitrile of* QUINOLINE CARBOXYLIC ACID.

CYANO-SUCCINIC ETHER $C_9H_{13}NO_2$ *i.e.* $CH(CN)(CO_2Et).CH_2.CO_2Et$. (158°) at 14 mm. Formed, together with cyano-tricarballylic ether, by the action of sodium on cyanoacetic ether dissolved in alcohol, the product being decomposed with chloro-acetic ether. Oil. Sol. alcohol, ether, and alkalis (Haller a. Barthe, *C. R.* 106, 1413).—$C_9H_{12}NaNO_2$.

CYANO-TEREPHTHALIC ACID $C_6H_3(CN)(CO_2H)_2$. From amido-terephthalic acid by cuprous cyanide and nitrous acid (Ahrens, *B.* 19, 1635). Amorphous yellow mass. Decomposed by boiling alkalis into trimellitic acid.

ω-**CYANO-*o*-TOLUIC ACID** $C_9H_7NO_2$ *i.e.* $CN.CH_2.C_6H_4.CO_2H$. [116°]. From phthalide and alcoholic KCy (W. Wislicenus, *A.* 233, 102), Crystalline powder (from HOAc). Aqueous KOH gives $CO_2H.CH_2.C_6H_4.CO_2H$. $CaA'_2$2aq.

β-**CYANO-*β*-*o*-TOLYLAMIDO-BUTYRIC ETHER** $CH_3.C(CN)(NHC_7H_7).CH_2.CO_2Et$. Formed by heating the cyanhydrin of aceto-acetic ether with *o*-toluidine (Schiller-Wechsler, *B.* 18, 1050).

α-**CYANO-*α*-*o*-TOLYLAMIDO-PROPIONIC ETHER** $CH_3.C(CN)(NHC_7H_7).CO_2Et$. [93°]. Formed by digesting *α*-cyano-*α*-oxy-propionic ether with *o*-toluidine in alcoholic solution. Small white needles; v. sol. benzene and warm alcohol, sl. sol. cold alcohol, insol. water (Gerson, *B.* 19, 2966).

α-**Cyano-*α*-*p*-tolylamido-propionic ether** $CH_3.C(CN)(NHC_7H_7).CO_2Et$: [81°]; glistering spangles; sol. alcohol and benzene, sl. sol. water

Formed by digesting α-cyano-α-oxy-propionic ether in alcoholic solution with *p*-toluidine (Gerson, *B.* 19, 2967).

γ-CYANO-VALERIC ACID $C_5H_9CyO_2$ *i.e.* $C_4H_8Cy.CO_2H$. [95°]. Formed by heating valerolactone to 290° with KCN. Prisms. Sol. water, $CHCl_3$, and C_6H_6. Gives, on saponification, α-methyl-glutaric acid (W. Wislicenus, *A.* 233, 114).

CYANPHENINE *v.* CYAPHENINE.

CYANPROPINE $C_{12}H_{21}N_3$. [115°]. S. ·063 at 23°. Formed by the action of sodium on butyronitrile under an extra pressure of about 20 cm. of mercury (E. v. Meyer, *J. pr.* [2] 37, 397). White prisms (from ether).

Reactions.—1. Is converted by heating with conc. HCl to 180° into $C_{12}H_{20}N_2O$, [97°], S. ·067 at 23°.—2. Gives with bromine in an acid solution the hydrobromide of bromocyanpropine from which ammonia liberates the base [80°].

Salt.—$(B'HCl)_2PtCl_4$. [97°]. Reddish-yellow prisms.

CYANURATES (metallic); and **SULPHO-CYANURATES** (metallic). Cyanuric acid is a polymeride of cyanic acid HNCO; it probably has the constitution $(CN)_3(OH)_3$.

CYANURATES. Cyanuric acid is tribasic; with most bases, however, it forms acid salts. Cyanurates of the alkalis and alkaline earths are sol. water, the others are insol., or only sl. sol.; the alkali cyanurates are decomposed by heat to HNCO, $(NH_4)NCO$, CO_2, N, and cyanate of the metal; the cyanurates are decomposed by H_2SO_4Aq or HNO_3Aq, giving $H_3N_3C_3O_3$.

Ammonium cyanurate $(NH_4)H_2.N_3C_3O_3.H_2O$; white lustrous prisms, which effloresce in air.

Barium cyanurates. (1) $Ba(H_2N_3C_3O_3)_2.2H_2O$; obtained by adding BaOAq to boiling $H_3N_3C_3O_3Aq$ till slight permanent pp. is formed; loses $2H_2O$ at 280°. (2) $Ba_2(HN_3C_3O_3)_2.3H_2O$; crystalline pp. by adding boiling $H_3N_3C_3O_3Aq$ to ammoniacal $BaCl_2Aq$ (Wohler, *A.* 62, 241).

Calcium cyanurate. Not obtained in definite form (Chevallier a. Lassaigne, *A. Ch.* [3] 13, 155).

Copper cyanurates. The normal salt $Cu_3(C_3N_3O_3)_2.H_2O$ is obtained by mixing acid Mg cyanurate with $CuSO_4Aq$; when $Na_3C_3N_3O_3Aq$ is used the salt $CuHC_3N_3O_3.3H_2O$ is obtained (Claus a. Putensen, *J. pr.* [2] 38, 208). C. a. P. also obtained the *basic salt* $(CuOH)_3.C_3N_3O_3.3H_2O$. The following *ammonio-copper cyanurates* are described: $Cu(HN_3C_3O_3).2NH_3.H_2O$ (W., *l.c.*); $Cu(H_2N_3C_3O_3)_2.2NH_3$ (Wiedemann, *P.* 74, 73); $Cu(H_2N_3C_3O_3)_2xNH_3$ where $x = 3$ and 4, and the *acid salt* $Cu(H_2N_3C_3O_3).H_3N_3C_3O_3.NH_3.H_2O$ (C. a. P., *l.c.*).

Lead cyanurate $Pb(HN_3C_3O_3)_2 3H_2O$; pp. obtained in microscopic prisms by dropping excess of basic Pb acetate into boiling $H_3N_3C_3O_3Aq$; decomposed to $(NH_4)CN$, $CO(NH_2)_2$, and Pb by heating in H (W., *l.c.*).

Potassium cyanurates. (1) $KH_2N_3C_3O_3$; by adding HClAq to crude K cyanate solution; difficultly sol. water (Liebig a. Wöhler, *P.* 20, 369; Campbell, *A.* 28, 52). (2) $K_2HN_3C_3O_3$; by adding alcohol to solution of the first salt, in presence of KOH; decomposed by water to KOH and the dihydrogen salt (L. a. W., *l.c.*).

Silver cyanurates. (1) $Ag_2HN_3C_3O_3$; pp. obtained by adding cyanuric acid to silver acetate in acetic acid (W., *l.c.*). (2) $Ag_3C_3N_3O_3$; by adding hot $AgNO_3Aq$ to hot $H_3N_3C_3O_3$ in NH_3Aq, and drying pp. at 300° (Liebig, *A.* 26, 123; Debus, *A.* 72, 20; *cf.* Wohler, *A.* 62, 241).

Silver-ammonium cyanurates. (1) $Ag_2HN_3C_3O_3.2NH_3$; formed by digesting the first Ag salt with NH_3Aq; loses all NH_3 on heating. (2) Another salt is described by Liebig (*A.* 26, 123; *cf.* Wohler, *A.* 62, 241), probably $Ag_2C_3N_3O_3.(NH_4)_3C_3N_3O_3.H_2O$.

Silver-potassium and *silver-lead cyanurates.* By boiling triargentic cyanurate with KOHAq a salt is formed, probably $Ag_2KC_3N_3O_3$ (W., *l.c.*). By boiling Pb cyanurate with excess of $AgNO_3Aq$, the salt $Ag_4Pb(C_3N_3O_3)_2.2H_2O$ is produced (W., *l.c.*).

Sodium cyanurate $Na_3C_3N_3O_3$; fine needles; separates on adding excess of hot NaOHAq to conc. $H_3C_3N_3O_3Aq$ (Hofmann, *B.* 3, 770).

SULPHOCYANURATES (Hofmann, *B.* 18, 2196). *Salts of sulphocyanuric acid,* $H_3C_3N_3S_3$. For an account of *sulphocyanuric acid v.* CYANIC (SULPHO) ACID and POLYMERIDES, p. 303.

Sodium sulphocyanurate $NaH_2C_3N_3S_3$; large crystals, e. sol. water; formed by digesting Na_2S with methyl sulphocyanurate. Sulphocyanurates of Cu, Pb, Li, K, and Ag are described.

DISULPHOCYANIDES (Fleischer, *A.* 179, 204). *Salts of disulphocyanic acid* $H_2S_2C_2N_2$ (*q. v.* p. 303, under CYANIC (SULPHO) ACID AND POLYMERIDES).

Potassium disulphocyanide $K_2S_2C_2N_2.H_2O$; obtained by adding an alcoholic solution of KOH to persulphocyanic acid, $H_2C_2N_2S_3$, and pressing the crystals which separate. Yellow monoclinic prisms; insol. absolute alcohol; v. sol. water; solution in water changes, quickly when heated, to K sulphocyanide. The other salts described by Fleischer (*l.c.*) are $BaS_2C_2N_2.2H_2O$; v. soluble, white rhombic prisms; $CuS_2C_2N_2$, brown-red pp. insol. dilute acids; $PbS_2C_2N_2$, citron-yellow pp. not acted on by dilute acids; $Ag_2S_2C_2N_2$, green pp.; $AgKS_2C_2N_2$, yellow, crystalline.

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CYANURIC ACID *v.* p. 319.

CYANURIC BROMIDE *v.* p. 320.

CYANURIC CHLORIDE *v.* p. 319.

CYANUROMALIC ACID $C_6H_6N_4O_4$. An unstable crystalline body formed by dissolving the cyanide of barbituric acid (*q. v.*) in aqueous KOH (Nencki, *B.* 5, 887).

CYAPHENINE $(C_7H_5N)_3$ *i.e.* Cy_3Ph_3. [230°]. (above 350°).

Formation.—1. By heating benzoyl chloride with KNCO (Cloez, *A.* 115, 27).—2. By heating benzonitrile bromide alone or with lime (Engler, *A.* 133, 146).—3. From benzonitrile and Na (Hofmann, *B.* 1, 194).—4. Traces are got from benzamide and $COCl_2$ (E. Schmidt, *J. pr.* [2] 5, 35). 5. From benzonitrile and $ZnEt_2$, the product being treated with alcohol and then with HCl (Frankland a. Evans, *C. J.* 37, 564).—6. From Cy_3Cl_3, bromo-benzene dissolved in ether, and sodium (Klason, *J. pr.* [2] 35, 82), Cy_3ClPh_2 [136°] being the chief product.

Preparation.—10 g. of benzonitrile are added gradually to 50 g. of slightly fuming H_2SO_4, kept cold. After 48 hours the liquid is slowly poured into 300 cc. water. The ppd. cyaphenine, after washing with water and alcohol, weighs 1·1 g. (A. Pinner, *J. pr.* [2] 30, 126; *B.* 11, 764).

Properties.—White branching crystals. Insol. water, v. sl. sol. alcohol and ether. Not affected by boiling KOH or HCl.

Reactions.—Heated in a sealed tube at 250° with conc. HCl it is entirely converted into benzoic acid and NH_3 (F. a. E.).

CYCLAMIN $C_{20}H_{36}O_{18}$ (?) [236°]. $[\alpha]_D = -11° 40'$ (in alcohol) (Michaud, *C. C.* 1887, 1397); $= -15°10'$ (Sachsse). Occurs in the roots of *Cyclamen europæum* and perhaps also of cowslips ('*Primulin*') (De Luca, *Cimento nuovo*, 5, 225; 8, 182; *G.* 2, 556; Martius, *Buchner's N. Repert.* 8, 388; Mutschler, *A.* 185, 214; Flückiger, *Ph.* [3] 8, 488). White amorphous substance (from alcohol). Irritates the throat. V. sol. boiling alcohol, insol. ether, chloroform, CS_2, and alkalis. Absorbs water from moist air, swelling up; slowly dissolves in water. The aqueous solution froths like soap, and is coagulated by heating. In contact with water it slowly decomposes forming glucose and mannite (De Luca, *C. R.* 87, 297). Aqueous HCl coagulates it and, at 80°, forms sugar. HOAc dissolves it and does not coagulate it on heating. It gives a white pp. with Fehling's solution, but does not reduce it even when hot. Conc. H_2SO_4 forms a red solution; on diluting with water glucose remains in solution, and there is ppd. white amorphous cyclamiretin $C_{15}H_{22}O_2$ [198°]. Chlorine water forms 'cyclamic acid' $C_{36}H_{56}O_{19}$(?) HNO_3 forms 'chrysolin' $C_{15}H_{21}NO_6$.

CYCLOPIC ACID $C_7H_8O_4$. Occurs in the leaves of *Cyclopia Vogelii* (Cape Tea). The aqueous decoction is digested with $Pb(OH)_2$, the lead compound suspended in dilute (50 p.c.) alcohol, and decomposed by H_2S. The filtrate is concentrated and mixed with alcohol and ether. Cyclopin is ppd.; cyclopic acid is obtained by evaporating the filtrate (Church, *C. N.* 22, 2; *Ph.* [3] 11, 693; Greenish, *Ph.* [3] 11, 569). Yellow needles, sol. water, insol. alcohol, ether, and CS_2. Aqueous alkalis form a yellow solution with green fluorescence. $FeCl_3$ gives a green colour, becoming brown on heating. Cupric acetate gives a grey pp. $K_2Cr_2O_7$ and HCl give a dark brownish-red colour.

Cyclopin $C_{25}H_{28}O_{13}$ **aq.** Obtained as above. Red substance, v. sol. water, insol. benzene, CS_2, ether, $CHCl_3$, and ligroin. Its aqueous solution decomposes on standing into glucose and cyclopin-red. KOH gives a brownish-red solution with green fluorescence. $FeCl_3$ gives an olive-green colour turned yellow by HCl and brown by NH_3. Ppts. salts of Cu, Pb, and Ag.

Cyclopin-red $C_{19}H_{22}O_{10}$. Formed as above. Sl. sol. water, ether, and benzene, v. sol. alcohol (when freshly ppd.). Alkalis dissolve it, forming red solutions. $FeCl_3$ gives a brown colour. $CaCl_2$ or alum followed by NH_3 gives a violet pp.

CYCLOTHRAUSTIC ACID $C_{17}H_{12}N_2O_3$ *i.e.* $[2:1]CO_2H.C_6H_4.NH.CO.C_9H_6N[$*Py.* 3]. [252°].

Formation.—α-Diquinoline is oxidised by $KMnO_4$ in presence of hot conc. AcOH. The pp. is filtered and digested with SO_2 until all the MnO_2 is converted into sulphate. After filtering again and well washing with hot water, the acid is dissolved in KOH. The K-salt is decomposed with weak H_2SO_4, washed, dried, recrystallised from boiling xylene, and decolourised with animal charcoal.

Preparation.—By heating dry anthranilic and quinaldinic acids together to 180° (Weidel a. Wilhelm, *M.* 8, 197).

Properties.—White woolly needles; insol. water, v. sl. sol. hot EtHO, Et_2O, $CHCl_3$, C_6H_6, and xylene; v. sol. hot AcOH and HCl.

S a l t s.—A'_2Ca 4aq: yellow flakes.—A'_2Ba aq.

Reactions.—1. With Ac_2O it forms an anhydride $C_{17}H_{10}N_2O_2$ [196°], crystallising in long colourless needles.—2. $KMnO_4$ in alkaline solution oxidises it to 'pyridanthrilic acid' $C_{15}H_{10}N_2O$, in acetic acid solution quinaldinic, α-oxyisocinchomeronic, and anthranilic acids are formed (Weidel a. Strache, *M.* 7, 285).

CYMENE $C_{10}H_{14}$ *i.e.* $C_6H_4MePr[1:4]$. *p-Propyl-toluene.* Mol. w. 134. (175°). V.D. 4·63 (calc. 4·65). S.G. $\frac{9\cdot8}{4}$ ·864 (Schiff, *A.* 220, 94); $\frac{20}{4}$ ·8569 (Brühl, *A.* 235, 19). C.E. (9·8 to 175·4°) ·001159 (S.). μ_α 1·494 (B.). μ_D 1·484 (Gladstone, *C. J.* 49, 623). H.C. 1401609 ($C, O_2 = 94$; $H_2, O = 69$) (Stohmann, *J. pr.* [2] 35, 41). S.V. 184·5 (Schiff); 181·62 (Ramsay).

Occurrence.—In the volatile oil of cumin (from *Cuminum Cyminum*); in the seeds of the water-hemlock (*Cicuta virosa*); in the oil of thyme; in oil of *Ptychotis Ajowan*; in Eucalyptus oil; and (to the extent of 6 p.c.) in oil of lemons (Gerhardt a. Cahours, *A. Ch.* [3] 1, 102, 372; *A.* 38, 101, 345; Trapp, *A.* 108, 386; Lallemand, *A. Ch.* [3] 49, 156; Haines, *C. J.* 8, 289; H. Muller, *B.* 2, 130; Faust a. Homeyer, *B.* 7, 1429; *Ar. Ph.* [3] 5, 385; Beilstein a. Kupffer, *B.* 6, 1181; *A.* 170, 282; Fittica, *A.* 172, 303; Tilden, *Ph.* [3] 9, 654).

Formation.—1. By the dehydration of camphor by means of P_2O_5, $ZnCl_2$, P_2S_5, or PCl_5 (Gerhardt, *A.* 48, 234; Delalande, *A.* 38, 342; Pott, *B.* 2, 121; Fittig, Kobrich, a. Jilke, *A.* 145, 129; Wright, *C. J.* 26, 686; Beckett a. Wright, *C. J.* 29, 1).—2. By heating dibromides of terpenes $C_{10}H_{16}Br_2$ with aniline (Oppenheim, *B.* 5, 94, 628).—3. By distilling crystallised terpin hydrate with Br (Barbier, *C. R.* 74, 194). 4. From thymol and P_2S_5.—5. From oil of turpentine and iodine (Kekulé a. Bruylants, *B.* 6, 437) or chlorine (Naudin, *Bl.* [2] 37, 111).—6. From oil of turpentine and H_2SO_4 or Et_2SO_4 (Riban, *Bl.* [2] 20, 100, 244; Wright, *C. J.* 26, 700; *C. N.* 29, 41; Paternò, *G.* 4, 113; Bruère, *C. R.* 90, 1428; Richter, *B.* 6, 1257).—7. From absinthol and P_2S_5 (Faust a. Homeyer, *B.* 7, 1427; Graebe, *B.* 5, 680; Beilstein a. Kupffer, *A.* 170, 282).—8. From menthene $C_{10}H_{18}$ and Br (Wright, *C. J.* 29, 1).—9. By boiling cuminic alcohol with zinc-dust (Kraut, *A.* 192, 224).—10. From *p*-bromo-toluene, *n*-propyl-bromide, and sodium (Fittig, Schäffer, a. Konig, *A.* 149, 334; Fittica, *A.* 172, 320; Jacobsen, *B.* 11, 2049).—11. According to Bouchardat (*C. R.* 90, 1560), cymene may be obtained from valerylene (derived from amyl alcohol) by heating it to 250° and treating the resulting divalerylene $C_{10}H_{16}$ with Br in CS_2.—12. By passing steam into cymene-sulphonic acid dissolved in diluted H_2SO_4 hydrolysis begins at 130° (Armstrong a. Miller, *C. J.* 45, 148).

Spectrum.—Absorption bands in ultra-violet, a narrow one at cadmium-line 17, and a broad band between Cd 17 and Cd 18. The first band enables the presence of cymene in essential oils to be detected and estimated, for it is visible when diluted with 20,000 volumes of alcohol, and examined in a column 15 mm. long (Hartley, *C. J.* 37, 676).

Reactions.—1. H_2SO_4 and $K_2Cr_2O_7$ give terephthalic acid.—2. Oxidised by air, in presence of aqueous NaOH, to cuminic acid. In this reaction Pr changes to Pr.—3. The urine of animals who have been given doses of cymene contains cuminuric acid, together with small quantities of cuminic acid (Jacobsen, *B.* 12, 1512; *cf.* Nencki a. Ziegler, *B.* 5, 749). Here, also, *n*-propyl becomes isopropyl.—4. $KMnO_4$ gives oxy-isopropyl-benzoic acid [c. 153°], as well as terephthalic acid (Remsen a. Emerson, *Am.* 8, 267). 5. HNO_3 forms *p*-tolyl methyl ketone and *p*-toluic acid. HNO_3 containing nitrous fumes forms '*β*-nitrocymene' $C_{18}H_{16}N_2O_4$ [125°] (Holleman, *R. T. C.* 6, 60).—6. Converted by Al_2Cl_6 at 150° into toluene and other products (Anschutz, *A.* 235, 191). Liquid compounds $(C_{10}H_{14})_3Al_2Cl_6$ and $(C_{10}H_{14})_3Al_2Br_6$ may be prepared (Gustavson, *J. R.* 11, 81). Al_2Br_6, in presence of Br, ultimately forms penta-bromo-toluene and isopropyl bromide (Gustavson, *B.* 10, 1101). In this reaction the PrBr first formed is changed by the Al_2Br_6 into PrBr.—7. By the action of CrO_2Cl_2, and treatment of the compound with water, it gives *p*-tolyl-propionic aldehyde (Richter a. Schuchner, *B.* 17, 1931; *cf.* Etard, *B.* 16, 2921; *A. Ch.* [5] 22, 258).

Cymene hexahydride $C_{10}H_{20}$. (172°). S.G. ^{17} ·812. Occurs in oil of resin (Renard, *A. Ch.* [6] 1, 230).

o-**Cymene** $C_6H_4PrMe[1:2]$. *o-Propyl-toluene.* (182° uncor.). From *n*-propyl bromide, *o*-bromo-toluene, and sodium (Claus a. Hansen, *B.* 13, 897).

m-**Cymene** $C_6H_4PrMe[1:3]$. *m-Propyl toluene.* (177°). S.G. ^{16} ·863. From *m*-bromo-toluene, *n* propyl bromide, and sodium (Claus a. Stusser, *B.* 13, 899).

m-**Isocymene** C_6H_4MePr [1:3]. (175°). S.G. ·865. Occurs in the essential oil obtained by distilling resin of fir trees (Kelbe, *A.* 210, 1; Renard, *A. Ch.* [6] 1, 249). Formed from toluene, isopropyl iodide and Al_2Cl_6 (Kelbe, *A.* 210, 1). Formed also, together with ordinary cymene, by the dehydration of camphor (Spica, *G.* 12, 543; Armstrong a. Miller, *B.* 16, 2258).

Preparation.—Essence of resin is washed with aqueous NaOH (to remove phenols), distilled with steam, shaken with dilute and afterwards with conc. H_2SO_4 in the cold, washed again with NaOH and distilled with steam. It is then sulphonated with a mixture of H_2SO_4 (4 pts.), and fuming H_2SO_4 (1 pt.) at 90°. The sodium salt of the iso-cymene sulphonic acid is decomposed by heating with conc. HCl for two days at 185°, and the liberated cymene distilled over with steam (Kelbe a. Warth, *A.* 221, 158).

Reactions.—1. *Oxidised* by chromic acid or permanganate to isophthalic acid (Zeigler a. Kelbe, *B.* 13, 1399).—2. Dilute HNO_3 forms *m*-toluic acid or aldehyde. Fuming HNO_3 forms a tri-nitro- derivative [72°].—3. CrO_2Cl_2 forms a chocolate-brown powder whence water liberates *m*-toluic acid.

p-**Isocymene** C_6H_4MePr [1:4]. (173°). S.G. ^{9} ·869; ^{25} ·862. From *p*-bromo-cumene, MeI, and sodium (Jacobsen, *B.* 12, 429; R. Meyer, *A.* 220, 27), or from isopropyl chloride, toluene, and Al_2Cl_6 (Silva, *Bl.* [2] 43, 321).

CYMENE-AZO-CYMENE *v.* AZO- COMPOUNDS

CYMENE-CARBOXYLIC ACID $C_6H_3MePrCO_2H$. [63°]. Prepared by fusing the amide with potash, or preferably by heating it with concentrated hydrochloric acid at 180°. Crystallises in slender needles isomeric with Rossi's homo-cuminic acid (Paternò a. Spica, *G.* 9, 400).

Amide $C_6H_3MePr.CONH_2$. [139°]. Formed from potassium cymene sulphonate by fusing with KCy and treating the resulting crude nitrile with alcoholic KOH (Paternò a. Fileti, *G.* 5, 30). Needles, sl. sol. cold water, v. sol. alcohol and ether.

m-**Cymene carboxylic acid** $C_6H_3MePr(CO_2H)$ [2:5:1]. [75°]. From the nitrile which is formed from tri-carvacryl phosphate and KCy (Kreysler, *B.* 18, 1714). Needles (from dilute alcohol). V. sl. sol. cold water.—AgA′.

Nitrile $C_6H_3MePrCN$. (245°).

CYMENE SULPHINIC ACID $C_6H_3MePr(SO_2H)$ [1:4:2]. From cymene sulphonic chloride, water, and zinc-dust. Syrup (Berger, *B.* 10, 977).—KA′ 3½aq.—AgA′.

CYMENE (α)-SULPHONIC ACID $C_6H_3MePr(SO_3H)$ [1:4:2]. Formed, together with the (*β*)-isomeride, by shaking cymene with conc. H_2SO_4 or $ClSO_3H$ at 90° (Gerhardt a. Cahours, *A. Ch.* [3] 1, 106; Delalande, *A. Ch.* [3] 1, 368; H. Muller, *B.* 2, 130; Jacobsen, *B.* 11, 1060; Claus a. Cratz, *B.* 13, 901; 14, 2141; Spica, *G.* 11, 201; *B.* 14, 652; Sieveking, *A.* 106, 260; Beilstein, *A.* 170, 287; Paternò, *B.* 7, 591; *G.* 3, 541, Kraut, *A.* 192, 226; Baur, *A.* 220, 18). Also formed by debromination of bromo-cymene sulphonic acid obtained from cymidine (Widmann, *B.* 19, 249).

Tables (from dilute H_2SO_4). The crystals contain 2aq and melt at 51° (S.) or 79° (C.); when anhydrous they melt at 220° (C.). The K salt is oxidised by $KMnO_4$ to oxy-isopropyl-sulpho-benzoic acid $C_6H_3(CO_2H)(SO_3H).CMe_2(OH)$. HNO_3 forms sulpho-*p*-toluic acid. Potash-fusion forms carvacrol. By treatment in aqueous solution with bromine it yields bromo-cymene $C_6H_3PrMeBr[4:1:2]$ and bromo-cymene-sulphonic acid $C_6H_2PrMeBr(SO_3H)[4:1:5:2]$ (Kelbe a. Koschnitzsky, *B.* 19, 1730).

Salts.—KA′ aq.—NaA′ 3aq (Paternò, *G.* 8, 291).—NaA′ 5aq.—BaA′$_2$ 3aq S. (of BaA′$_2$) 2·5 at 12° (S.). Pointed leaflets, crystallising readily; m. sol. 90 p.c. alcohol.—CaA′$_2$ 2aq: monoclinic crystals, $a:b:c = 1{\cdot}374:1:1{\cdot}121$; $\beta = 95°\ 13'$ (Jerofejeff, *A.* 170, 297).—PbA′$_2$ 3aq. S. (of PbA′$_2$) 1·3 to 1·9.—NiA′$_2$ 5aq.

Amide $C_6H_3MePr(SO_2NH_2)$. [112°] (J.); [116°] (Kelbe, *B.* 19, 1969).—$C_6H_3MePr(SO_2NHAg)$ (Berger, *B.* 10, 976).

Benzoyl-amide $C_6H_3MePr(SO_2NHBz)$. [153°] (Wolkoff, *B.* 5, 142).

Cymene (β)-sulphonic acid $C_6H_3MePr(SO_3H)$ [1:4:3]. [131°]. Formed, in small quantity, in the sulphonation of cymene (Claus a. Cratz, *B.* 13, 901; 14, 2141). Formed also by debromination of bromo-cymene sulphonic acid (Remsen a. Day, *Am.* 5, 154; *v. also* Kelbe a. Koschnitzky, *B.* 19, 1730; Claus a. Christ, *B.* 19, 2165). Granules; extremely sol. water, sol. alcohol, insol. ether.

Salts.—NaA′aq. — KA′aq. — CaA′$_2$$x$aq. — BaA′$_2$3aq (over H_2SO_4). Gelatinous; v. e. sol. water, sol. alcohol.—PbA′$_2$3aq: amorphous, v. e. sol. water.—CuA′$_2$aq.

Amide $C_6H_3MePr.SO_2NH_2$. [148°].

o-**Cymene (α)-sulphonic acid** $C_6H_3MePr(SO_3H)$ [1:2:x]. Formed, together with the following, by sulphonating *o*-cymene, especially at low temperatures (Claus a. Hansen, *B.* 13, 897).—KA′½aq. BaA′aq: stellate groups of laminæ.—CuA′$_2$4aq.

o-**Cymene (β)-sulphonic acid** $C_6H_3MePr(SO_3H)$ [1:2:x]. Formed as above.—BaA′$_2$$x$aq: gelatinous mass, v. e. sol. water.

Amide. Very slender needles (from water).

m-**Cymene (α)-sulphonic acid** $C_6H_3MePr(SO_3H)$ [1:3.x]. Formed, together with the (β)-isomeride, by warming *m*-cymene with conc. H_2SO_4 (Claus a. Stusser, *B.* 13, 899).—KA′.—CaA′$_2$2aq.—BaA′$_2$aq: laminæ. S. (of BaA′$_2$) ·43 at 17°.—PbA′$_2$3aq.—CuA′$_2$4aq.

m-**Cymene (β)-sulphonic acid** $C_6H_3MePr(SO_3H)$ [1:3:x]. Formed as above.—BaA′$_2$aq: needles. S. (of BaA′$_2$) 3·83 at 16°.

m-**Isocymene (α)-sulphonic acid** $C_6H_3MePr(SO_3H)$ [1:3:6]. [89°]. Formed, together with the (β)-isomeride, by treating isocymene with conc. H_2SO_4 (Kelbe, *A.* 210, 30; *B.* 15, 39; Spica, *G.* 12, 187, 546). Deliquescent micaceous leaflets. Br in the cold gives bromo-isocymene sulphonic acid, but at 40° it forms (6,1,3)-bromo-isocymene. KOH and $KMnO_4$ gives oxy-isopropyl-sulpho-benzoic acid.

Salts. NaA′aq.—KA′3aq.—KA′ (Armstrong a. Miller, *B.* 16, 2258).—BaA′$_2$aq: pearly plates, v. sl. sol. cold, sl. sol. hot, water. S. ·37 (Spica). BaA′$_2$: plates (Boner, *A.* 220, 33). PbA′$_2$aq. S. 1·3 at 22° (Spica).—CuA′$_2$2aq.—CuA′$_2$4aq.—NiA′$_2$5aq.

Amide $C_6H_3MePr.SO_2NH_2$. [73°] (K.); [75°] (S.). Laminæ, sl. sol. boiling water.

m-**Isocymene (β)-sulphonic acid** $C_6H_3MePr(SO_3H)$ [1:3:4].

Formation.—1. By sulphonation of isocymene.—2. By sulphonation of (α)-bromo-isocymene and removal of the Br by sodium amalgam (Kelbe a. Czarnomski, *B.* 17, 1746; *A.* 235, 285).

Salts.—NaA′3aq.—BaA′$_2$8aq: laminæ, v. e. sol. water.—CaA′$_2$5½aq. CuA′$_2$3½aq.—PbA′$_2$8aq.

Amide $C_{10}H_{13}(SO_2NH_2)$ [162°].

p-**Iso-cymene (α)-sulphonic acid** $C_6H_3MePr(SO_3H)$ [1:4:2]. From iso-cymene and H_2SO_4, together with the (β)-isomeride (Jacobsen, *B.* 12, 431). KOH and potassium permanganate converts it into oxy-propyl-sulpho-benzoic acid $C_6H_3(CO_2H)(C(OH)Me_2)SO_3H$ (R. Meyer a. H. Boner, *A.* 220, 30). Potash-fusion gives oxy-terephthalic acid and oxy-cuminic acid [88°].

Salts.—BaA′$_2$aq: slender needles. S. 4·28 at 0°.—CuA′$_2$4aq: blue leaflets.

Amide $C_6H_3MePr(SO_2NH_2)$. [98°].

p-**Isocymene (β)-sulphonic acid** $C_6H_3MePr(SO_3H)$. Formed as above. Its Ba salt is extremely soluble in water.

Amide $C_6H_3MePr(SO_2NH_2)$. [80°–90°].

Cymene disulphonic acid $C_6H_2MePr(SO_3H)_2$. From cymene and fuming H_2SO_4 (Kraut, *A.* 192, 226).—BaA″aq: v. e. sol. water (Claus, *B.* 14, 2140).

m-iso-**CYMENOL** $C_6H_3PrMe(OH)$ [4:2:1]. *Methyl-isopropyl-phenol m-isocymophenol.* (231°). R_∞ 1·52. From *m*-isocymene sulphonic acid (1 pt.) by fusion with KOH (6 pts.) (Kelbe, *A.* 210, 40). Liquid, smelling like thymol. Gives a violet colour with $FeCl_3$. By KOH fusion it is converted into *o*-oxy-isophthalic acid and *p*-cuminol-carboxylic acid $C_6H_3Pr(OH)CO_2H$ [4:1:2].

Benzoyl derivative $C_6H_3PrMe(OBz)$. [73°]. Monoclinic crystals; $a:b:c$ = ·52:1:·82; β = 82° 17′.

Methyl ether $C_6H_3PrMe(OMe)$: (217°).

Ethyl ether $C_6H_3PrMe(OEt)$: (224°).

Tri-bromo-derivative $C_6Br_3PrMe(OH)$: [222°]; plates (Jesurun, *B.* 19, 1413).

Isomerides: CARVACROL and THYMOL.

m-iso-**CYMENOL-CARBOXYLIC ACID** $C_6H_2PrMe(OH)CO_2H$ [1:3:4:5]. *Cymenotic acid.* [147°]. Formed by the action of CO_2 upon sodium *m-iso*-cymenol (*m*-isopropyl-phenol). Long slender needles (from hot water). Sl. sol. hot water, nearly insol. cold water. Fe_2Cl_6 produces a bluish-violet colouration.

Salts.—AgA′: small needles, m. sol. hot water.—BaA′$_2$4aq: needles, v. sol. alcohol.

Methyl ether A′Me: [118°]: short needles (from alcohol) (Jesurun, *B.* 19, 1414).

Isomerides: CARVACROTIC and THYMOTIC ACIDS

CYMIDINE $C_6H_3(C_3H_7)(CH_3)NH_2$ [4:1:3].

Preparation.—Nitro-cymylene-dichloride $C_6H_3(C_3H_7)(NO_2)(CHCl_2)$, obtained by the action of PCl_5 on nitrocuminic aldehyde, is reduced with zinc and HCl.

Properties.—Colourless oil. Volatile with steam. Sol. alcohol and ether. Stable towards oxidising agents. By nitrous acid it is converted into thymol.

Salts.—B′HCl: fine needles.—$(B'HCl)_2PtCl_4$: sparingly soluble yellow needles.—$B'_2H_2SO_4$2½aq: small white needles, sl. sol. cold water.

Acetyl derivative. [about 112°]. White needles (Widman, *B.* 15, 167; 21, 2126; *cf.* Barlow, *A.* 98, 248; *P. M.* [4] 10, 451).

Cymidine $C_6H_3PrMe(NH_2)$ [4:1:2]. From (2,4,1)-nitro-cymene (Lóderbaum, *B.* 21, 2127).—B′HCl.—$B'_2H_2SO_4$aq.

m-**Isocymidine** $C_6H_3PrMe(NH_2)$ [3:1:5 or 6]. (233°). From nitro-iso-cymene (Kelbe a. Warth *A.* 221, 163). Yellowish oil. V. sl. sol. water, v. sol. alcohol, light petroleum, or benzene.

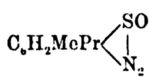
Salts.—$B'_2H_2SO_4$. Sl. sol. water.—$B'H_2C_2O_4$.

Acetyl derivative $C_6H_3PrMeNHAc$ [118°].

Benzoyl derivative $C_6H_3PrMeNHBz$. [165°].

Phthalyl derivative $C_6H_4C_2O_2NC_6H_3PrMe$. [145°].

(?*n*)-**CYMIDINE-SULPHONIC ACID** $C_6H_2Me(C_3H_7)(NH_2)SO_3H$ [1:4:3:6]. Formed by heating cymidine with fuming H_2SO_4. Thin glistening colourless plates or prismatic needles. V. sl. sol. cold water. Insol. alcohol. Is probably a *n*-propyl-derivative, since by treatment of the diazo- compound with HBr and debromination it gives rise to the sulphonic acid of *n*-cymene. The corresponding


Diazo- compound $C_6H_2MePr\left<\begin{matrix}SO_3\\ |\\ N_2\end{matrix}\right.$ forms small white needles, v. e. sol. water, sl. sol. alcohol, insol. ether. By warming with absolute alcohol it is converted into the sulphonic acid of the ethyl-ether of thymol (Widmann, *B.* 19, 246)

Isocymidine sulphonic acid $C_6H_2MePr(NH_2)(SO_3H)$. From amido-iso-cymene and fuming H_2SO_4 (Kelbe a. Warth, *A.* 221, 177).

Salt.—BaA'_2.

CYMINYL. Also called Cymyl (*q. v.*).

CYMOPHENOL *v.* Cymenol.

CYMOPHENONE *v.* Phenyl cymyl ketone.

CYMYL. The radicle $C_6H_3Me(C_3H_7)$. Its derivatives are described below; see also Carvacryl and Thymyl compounds. Cuminyl $C_6H_4(C_3H_7)CH_2$ is isomeric with cymyl.

CYMYLAMINE *v.* Thymylamine and Carvacrylamine.

ISOCYMYL-CARBAMIC ETHER $C_6H_3PrMeNH.CO_2Et$. [229°]. From $ClCO_2Et$ and amido-iso-cymene. Slender needles (from alcohol).

ISOCYMYL CARBAMINE $C_6H_3PrMeNC$. From amido-iso-cymene, KOH, $CHCl_3$, and alcohol (Kelbe a. Warth, *A.* 221, 170). Oil of very nasty odour, nearly insol. water, sol. alcohol, ether, and benzene. Can be distilled with steam, but not alone at ordinary pressure.

DI-CYMYL ETHYLENE DIKETONE $(C_6H_3MePr.CO)_2C_2H_4$. (c. 320°). From cymene, succinyl chloride, and $AlCl_3$ (Claus, *B.* 20, 1378).

ISOCYMYL ETHYL GUANIDINE

$C_6H_3PrMeNH.C(NH).NHEt$.

From $C_6H_3PrMeNH.CS.NHEt$, alcoholic NH_3, and PbO (K. a. W.). Gummy mass.

Tribenzoyl derivative $C_6H_3PrMeNBzC.(NBz).NBzEt$. [165°]. Needles (from alcohol).

CYMYL ETHYL KETONE CARBOXYLIC ACID $C_6H_3(C_3H_7)Me.CO.CH_2.CH_2.CO_2H$. From cymene, succinyl chloride, CS_2, and Al_2Cl_6 (Claus, *B.* 20, 1378).—PbA'_2.

ISOCYMYL ETHYL THIO-UREA $C_6H_3PrMeNH.CS.NHEt$. *Methyl-iso-propyl-phenyl-thio-ethyl-urea.* Formed by heating amido-iso-cymene with ethyl-mustard oil. An amorphous gummy mass (K. a. W.).

CYMYL METHYL KETONE $CH_3.CO.C_6H_3MePr$ [1:2:5]. (248°). From cymene, AcCl, and $AlCl_3$ (Claus, *B.* 19, 232).

DI-ISOCYMYL THIO-UREA $(C_6H_3PrMeNH)_2CS$. [160°]. From amido-iso-cymene and CS_2 in a sealed tube at 100° (K. a. W.). Slender needles (from alcohol).

ISOCYMYL-UREA $NH_2.CO.NH.C_6H_3PrMe$. *Eso-methyl-eso-iso-propyl-phenyl-urea.* [176°]. From KNCO and amido-iso-cymene sulphate (Kelbe a. Warth, *A.* 221, 171). Matted glittering needles (from water).

Di-isocymyl-urea $CO(NH.C_6H_3PrMe)_2$. From $COCl_2$ and amido-iso-cymene in ether. Slender needles (from alcohol).

CYNANCHOL. A crystalline substance extracted by Butlerow (*A.* 180, 349) from *Cynanchum acutum*, a creeping plant growing near the Oxus, and said to poison camels. According to Hesse (*A.* 182, 163) it is a mixture of cynanchocerin [146°] and cynanchin [149°].

CYNAPINE. A reddish-yellow oil with powerful odour, contained in the seeds of fool's parsley (*Æthusa Cynapium*), whence it may be extracted by distilling with milk of lime. Strongly alkaline in reaction (Ficinus, *Mag. Pharm.* 20, 357; Bernhardt, *Ar. Ph.* [3] 16, 117).

CYNENE *v.* Cinene.

CYNEOL *v.* Cineol.

CYNURENIC ACID is Oxy-quinoline carboxylic acid (*q. v.*).

CYNURIC ACID $C_9H_7NO_5$ *i.e.* $CO_2H.C_6H_4.CO.CO_2H$. *Oxaloxyl-o-amido-benzoic acid.* [189°]. S. 1·12 at 10°. Formed by oxidising cynurenic acid, acetyl-quinoline tetrahydride, or carbostyril by alkaline $KMnO_4$ (Kretschy, *M.* 4, 157; Friedlander a. Ostermaier, *B.* 15, 332). Formed also by heating dry oxalic acid with *o*-amido-benzoic acid at 130° (Kretschy *M.* 5, 21). Needles (from ether). Fe_2Cl_6 colours its aqueous solution crimson. Boiling acids and alkalis split it up into oxalic and *o*-amido-benzoic acids.

Salts.—$KHA''\frac{1}{2}aq$.—$(NH_4)_2A''$.—$BaH_2A''_2aq$. $BaA''aq$.—$CaA''2\frac{1}{2}aq$.—$Cu_4A''_2O\,4aq$.—Ag_2A''.

Ethyl ether EtA'. [181°]. From indoxylic ether and chromic mixture (Baeyer, *B.* 15, 778). Needles (from alcohol).

CYSTEÏN $C_3H_7NSO_2$ *i.e.* $CH_3.C(NH_2)(SH).CO_2H$. Prepared by adding tin to a solution of cystin in hydrochloric acid (Baumann, *H.* 8, 299). Crystalline powder, sol. water, ammonia, and acids. The aqueous solution is oxidised to cystin even by the air.

CYSTIN $C_6H_{12}N_2S_2O_4$ *i.e.* $S(CMe(NH_2).CO_2H)_2$. $[\alpha]_D = -206°$ in 11 p.c. HClAq (Mauthner, *H.* 7, 225); $[\alpha]_j = -142°$ in NH_3Aq (Kulz, *Z. B.* 20, 1). Occasionally occurs as urinary calculus or sediment (Wollaston, *P. T.* 1810, 223; Golding Bird, *Treatise on Urinary Concretions*; Toel, *A.* 96, 217; Lassaigne, *A. Ch.* [2] 23, 328; Baudrimont a. Malaguti, *J. Ph.* 24, 633; Thaulow, *A.* 27, 197; Marchand, *J. pr.* 16, 254; Robert, *J. Ph.* 7, 165; O. Henry, *J. Ph.* 23, 11; Taylor, *P. M.* [3] 12, 337; Niemann, *A.* 187, 101; Udranszky a. Baumann, *B.* 21, 2744). Found also in the kidneys of the ox (Cloetta, *A.* 99, 299) and in the liver of a drunkard who died of typhus fever (Scherer, *N. Jahrb. Pharm.* 7, 306). In very small quantities it is a normal constituent in urine (Goldmann a. Baumann, *H.* 12, 254).

Properties.—Neutral and tasteless. Crystalline mass. Insol. water and alcohol; sol. aqueous ammonia (difference from uric acid) and potash, and reppd. as six-sided laminæ by HOAc. Sol. HClAq. Separates from an ammoniacal solution as colourless laminæ. Cold ammoniacal $AgNO_3$ followed by HNO_3 gives a canary yellow pp., but hot ammoniacal $AgNO_3$ ppts. Ag_2S (Dewar a. Gamgee, *Ph.* [3] 1, 385). Baryta-water at 150° gives barium sulphide and sulphite. Nitrous acid forms pyruvic acid (Dewar a. Gamgee, *Ph.* [3] 3, 144; *H.* 5, 329). Boiling aqueous NaOH converts part of its S into H_2S.

Benzoyl derivative $C_6H_{10}Bz_2N_2S_2O_4$. [158°]. Its Na derivative is ppd. by adding BzCl to a solution of cystin in aqueous NaOH. Slender needles. Strong acid, insol. water, sl. sol. ether, m. sol. alcohol (G. a. B.).

CYTISINE $C_{20}H_{27}N_3O$. [155° cor.]. An alkaloid occurring in the unripe seeds of the laburnum, *Cytisus Laburnum* (Chevallier a. Lassaigne, *J. Ph.* 4, 340; 7, 235; Peschier, *J. Chim. Méd.* 6, 65; Husemann a. Marmé, *Z.* [2] 1, 161; 5, 677). Crystalline mass (from alcohol) or thin needles and laminæ (by sublimation). V. e. sol. water and alcohol, nearly insol. ether, benzene, and chloroform. Expels NH_3 from its salts, even in the cold. Poisonous. Does not reduce Fehling's solution. Potassio-mercuric iodide gives a white flocculent pp. becoming crystalline. I in KI gives an amorphous red pp. changing to prisms. Bromine-water gives an orange pp. even in very dilute (1:15000) solutions. Sodium phosphomolybdate gives a yellow pp. Tannin forms a pp. only after neutralisation with NaOH. Picric acid gives a yellow pp. soon becoming crystalline.

Colour tests.—Conc. H_2SO_4 gives no colour. Sulphomolybdic acid reaction gives no colour. H_2SO_4 and $K_2Cr_2O_7$ a yellow turning brown. HNO_3 an orange-yellow.

Salts.—$B'(HNO_3)_2$ 2aq: prisms, with bitter taste.—$B'H_3Cl_3$ *x*aq.—$B'H_2PtCl_6$.—$B'H_4PtCl_8$.—$B'(HAuCl_4)_2$.—$B'Hg_2Cl_4$.

D

DAMALURIC ACID $C_6H_{10}O_2$. [53°]. An acid said to have been obtained from cows' urine (Städeler, *A.* 77, 27; Werner, *Z.* [2] 4, 413).

DAMBONITE $C_8H_{16}O_6$. [190°]. *Di-methyl-dambose. Di-methyl-inosite.* Occurs in a peculiar kind of caoutchouc. Exported from Gaboon in West Africa (Girard, *C. R.* 67, 820). Six-sided prisms (from alcohol), oblique prisms (containing 3aq) (from water), or slender needles (by sublimation). Not affected by dilute acids or alkalis, by Fehling's solution, or by fermentation. HI gives MeI and dambose, identical with inosite. KI forms crystals of $C_8H_{16}O_6KI$. HNO_3 and H_2SO_4 form an explosive nitrate (Champion, *C. R.* 73, 114).

Acetyl derivative $C_8H_{12}Ac_4O_6$. [193°]. (337°). Needles (Maquenne, *A. Ch.* [6] 12, 566; *C. R.* 104, 1853).

Benzoyl derivative $C_8H_{12}Bz_4O_6$. [250°]. Minute pale-yellow needles (M.).

DAMBOSE $C_6H_{12}O_6$. [218°]. Obtained by heating dambonite with aqueous HI at 120° (Girard, *C. R.* 67, 820; 73, 426; 77, 995). According to Maquenne (*C. R.* 104, 1853) it is identical with inosite (*v.* INOSITE and SUGARS). Six-sided prisms (from dilute alcohol); monoclinic prisms (containing 2aq) (from water). Inactive. V. e. sol. water, insol. absolute alcohol. Not prone to fermentation.

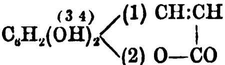
Hexa-acetyl derivative $C_6H_6Ac_6O_6$ [211°].

Methyl ether $C_6H_{11}MeO_6$. *Bornesite.* [175°]. In caoutchouc from Borneo (Girard, *Z.* [2] 7, 335).

Di-methyl ether v. DAMBONITE.

DAMMARA RESIN. New Zealand Kauri gum, the gum-resin from *Dammara australis* contains a slightly lævorotatory terpene dammarole $C_{10}H_{16}$ (158°) S.G. $\underline{15}$ ·863 (Rennie, *C. J.* 39, 240; *cf.* Thomson, *A. Ch.* [3] 9, 499; Muir, *C. J.* 27, 733). Dammar-Puti or East Indian dammara resin may be separated, according to Dulk (*J. pr.* 14, 16), by successive treatment with weak alcohol, absolute alcohol, and ether into hydrated dammarylic acid $C_{45}H_{74}O_4$ [50°], anhydrous dammarylic acid $C_{45}H_{72}O_3$ [60°], and dammaryl $C_{45}H_{72}$ [190°], the residue being $C_{90}H_{144}O$ [215°]. Franchimont obtained an acid $C_{30}H_{52}O_7$. See also Schrötter, *P.* 59, 37.

DANAÏN $C_{11}H_{14}O_5$. Said to occur in the root of *Danaïs fragrans*, and to give by hydrolysis a sugar and resinous danaïdin (Schlagdenhauffen, *J.* 1885, 1815).

DAPHNETIN 

$$C_6H_2\overset{(3\,4)}{(OH)_2}\left\langle\begin{array}{l}(1)\ CH{:}CH\\ \qquad\quad\ \ |\\ (2)\ O{-}CO\end{array}\right.$$

. *Di-oxy-coumarin.* [256°]. Prepared by hydrolysis of daphnin, a glucoside occurring in the bark of *Daphne alpina* and *Daphne Mezereum* (Zwenger, *A.* 115, 8; Stünkel, *B.* 12, 109).

Synthesis.—By heating molecular proportions of pyrogallol and malic acid with H_2SO_4 (twice the weight of the former), and precipitating the melt in cold water (Pechmann, *B.* 17, 938).

Properties.—Needles or prisms. Sol. hot water, sl. sol. ether, nearly insol. chloroform, benzene, and CS_2. Dissolves in alkalis with a reddish-yellow colour.

Reactions.—Fe_2Cl_6 gives a green colouration which changes to red on adding Na_2CO_3. Potassic ferricyanide and NH_3 gives a reddish-yellow colour. HNO_3 gives an intense red. It reduces $AgNO_3$ and Fehling's solution in the cold. Baryta water, $Zn(OAc)_2$, and $Pb(OAc)_2$ give yellow pps. After boiling with $NaHSO_3$, Fe_2Cl_6 gives an intense blue colour.

Di-acetyl derivative $C_9H_4O_2(OAc)_2$: [129°]; colourless needles, insol. water, sol. other solvents.

Di-benzoyl derivative $C_9H_4O_2(OBz)_2$: [152°]; fine needles, insol. water and ether, sparingly soluble in alcohol (Pechmann, *B.* 17, 933).

Mono-ethyl ether $C_9H_5O_3(OEt)$: [155°]; colourless glistening plates, v. sol. alcohol, ether, benzene, and aqueous alkalis, sl. sol. water.

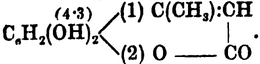
Di-ethyl ether $C_9H_4O_2(OEt)_2$: [72°]; colourless needles. V. sol. alcohol, ether, and benzene, insol. water and aqueous alkalis (Will a. Jung, *B.* 17, 1081).

Bromo-daphnetin $C_9H_5BrO_4$.

Di-ethyl ether $C_9H_3BrO_2(OEt)_2$: [115°]; colourless feathery crystals. Sol. hot alcohol, ether, and benzene, sl. sol. cold alcohol, insol. aqueous alkalis. Formed by bromination of the di-ethyl ether of daphnetin. By boiling with alcoholic KOH it is converted into the di-ethyl-derivative of daphnetilic acid (Will a. Jung, *B.* 17, 1084).

Tetra-bromo-daphnetin. *Acetyl derivative* $C_9HBr_4AcO_4$. [c. 290°]. From acetyl-daphnetin and Br at 100° (Stünkel).

β-Methyl-daphnetin



$$\overset{(4\cdot3)}{C_6H_2(OH)_2}\left\langle\begin{array}{l}(1)\ C(CH_3){:}CH\\ \qquad\qquad\qquad |\\ (2)\ O \text{ ——— } CO\end{array}\right.$$

. Formed by the action of H_2SO_4 on a mixture of aceto-acetic ether and pyrogallol. By boiling with sodium bisulphite till dissolved and then adding Fe_2Cl_6 a blue colouration is produced (Pechmann a. Cohen, *B.* 17, 2188).

Daphnetic acid $C_6H_2(OH)_3.CH{:}CH.CO_2H$. *Tri-oxy-cinnamic acid.*

Tri-ethyl derivative $C_6H_2(OEt)_3.C_2H_2.CO_2H$: [193°]; colourless crystals. V. sol. hot alcohol, ether, and benzene, insol. water and CS_2. Obtained by evaporating the di-ethyl-ether of daphnetin with aqueous NaOH, and heating the residue with ethyl iodide. On oxidation with $KMnO_4$ it gives tri-ethoxy-benzoic aldehyde and acid (Will a. Jung, *B.* 17, 1086).

Daphnetilic acid $C_8H_3O(OH)_2.CO_2H$.

Di-ethyl derivative $C_8H_3O(OEt)_2.CO_2H$. [154°]. Fine felted needles. Formed by boiling the di-ethyl ether of bromo-daphnetin with alcoholic KOH (Will a. Jung, *B.* 17, 1085).

DAPHNIN $C_{15}H_{16}O_9$. [c. 200°]. A glucoside occurring in the bark of certain species of Daphne (Vauquelin, *A. Ch.* 84, 173; Gmelin a. Baer, *Sch. J.* 35, 1; Zwenger, *A.* 115, 1). Rectangular prisms (containing 2aq) (from water). Sl. sol. cold water, v. sol. boiling alcohol, insol. ether. Alkalis and alkaline carbonates dissolve it, forming a yellow solution, which turns brown in air. Fe_2Cl_6 colours its aqueous solution bluish. It slowly reduces boiling Fehling's solution. Hot solutions are ppd. by basic lead acetate. Emulsin or dilute acids split it up into glucose and daphnetin.

DATISCIN $C_{21}H_{22}O_{12}$. [180°]. A glucoside occurring in the leaves and roots of *Datisca cannabina*, which are used to dye silk yellow (Braconnot, *A. Ch.* [2] 3, 277; Stenhouse, *Chem. Gaz.* 1856, No. 318; *A.* 98, 166). Silky needles, sl. sol. cold water, v. sol. alcohol, v. sl. sol. ether. Tastes bitter. Resolved by dilute acids into glucose and datiscetin. Bases dissolve it with deep-yellow colour. Lead acetate, Fe_2Cl_6, $CuSO_4$, and $SnCl_4$ ppt. its solution.

Datiscetin $C_{15}H_{10}O_6$. Formed as above. Tasteless needles, nearly insol. water, v. e. sol. ether.—$C_{15}H_8PbO_6$.

DATURINE is identical with Atropine (*q.v.*).

DAVYUM. According to Kern, some specimens of Russian platinum ores contain a metal which is not Ir, Os, Pd, Pt, Rh, nor Ru (*C. N.* 36, 114). The mother-liquor remaining after separation of Rh and Ir by Bunsen's method (*P. M.* [4] 36, 253) was heated with excess of NH_4Cl and NH_4NO_3; the dark-red pp. thus obtained was strongly heated, whereby the new metal was obtained as a spongy mass, which fused in the O-H flame to a silver-white button. The ore contained about ·045 p.c. of the new metal, to which Kern gave the name *Davyum.* The metal is described as hard, but malleable when heated; e. sol. *aqua regia*, v. sl. sol. boiling H_2SO_4. S.G. 9·389. At. w. about 154. Several salts of this metal are described by Kern. The whole subject requires re-investigation.

M. M. P. M.

DECACRYLIC ACID *v.* Decenoic acid.

DECANAPHTHENE *v.* Decylene.

n-**DECANE** $C_{10}H_{22}$. (169°–170°) at 742 mm.; (107°) at 100 mm. S.G. $\frac{0}{4}$ ·745; $\frac{15}{4}$ ·734; $\frac{100}{4}$ ·669. S. (glacial acetic acid) 8 at c. 15°; 20 at 60°. From *n*-octyl bromide, EtBr and Na (Lachowicz, *A.* 220, 179). Formed also from methyl ennyl ketone by treatment with PCl_5 and reduction of the product by HI and P; and by reducing octoic acid with HI and P (Krafft, *B.* 15, 1695). Has hardly any smell and no taste. Not attacked by conc. H_2SO_4. Attacked by Br only when heated.

Decane $C_{10}H_{22}$. *Inactive di-isoamyl.* (158·8° cor.) at 732·8 mm. S.G. $\frac{22}{}$ ·7216 (Lachowicz, *A.* 220, 172). V.D. 72 (for 71). S. (in glacial acetic acid) 8 at c. 15°; 20 at 65°. S.V. 231·3 (Schiff, *A.* 220, 88). From isoamyl iodide and zinc (Frankland, *C. J.* 3 32). From isoamyl bromide or iodide and sodium (Wurtz, *A. Ch.* [3] 44, 275; Grimshaw, *B.* 10, 1602; *C. J.* 32, 260, 687). Formed also by the electrolysis of sodium hexoate (Brazier a. Gossleth, *C. J.* 3, 221). Tasteless, with faint odour. Flashing-point 53°. Not attacked by HNO_3 or conc. H_2SO_4. Gives with bromine decyl bromide, which on distillation splits up into decylene and HBr.

Decane $CHMeEt.CH_2.CH_2.CHMeEt$. *Active diamyl.* (160°). V.D. 4·82 (for 4·91). S.G. $\frac{22}{22}$ ·7463. $[\alpha]_D = 6\cdot49^\circ$ for 100 mm. at 22°. From active amyl iodide and sodium (Just, *A.* 220, 155).

Decane (152°–153°). S.G. $\frac{21}{}$ ·7187. V.D. 69·4 (for 71). In Galician petroleum (Lachowicz, *A.* 220, 195).

Another **decane** from same source: (162°–163°). S.G. $\frac{20}{}$ ·7324.

Decane $C_{10}H_{22}$. (160°) (Pelouze a. Cahours, *A. Ch.* [4] 1, 5); (156°) (Wurtz, *Bl.* 1863, 300; Lemoine, *Bl.* [2] 41, 165). S.G. $\frac{16}{}$ ·757 (P. a. C.); " ·764 (L.). V.D. 4·95. Occurs in American petroleum.

Decane. (171°). S.G. $\frac{15}{}$ ·756. In coal tar (Jacobsen, *A.* 184, 202).

DECARBUSNIC ACID *v.* Usnetic acid.

DECENE *v.* Decylene.

DECENOIC ACID $C_{10}H_{18}O_2$ *i.e.* $C_6H_{13}.CH{:}CH.CH_2.CO_2H$. [10°]. Formed by distilling the lactone of β-oxy-heptyl-succinic acid (*q. v.*). Oil, hardly soluble in, and lighter than, water. Volatile with steam. Combines with HBr (Schneegans, *A.* 227, 91).

Salts.—BaA'_2.—CaA'_2.—AgA'.

Decenoic acid $C_{10}H_{18}O_2$. *Amenyl-valeric acid.* (269°). S.G. $\frac{12}{}$ ·961. From sodium isoamylate and CO at 165° (Fröhlich a. Geuther, *A.* 202, 297). Oil. The Na salt is deliquescent.

Decenoic acid $C_{10}H_{18}O_2$. *Amydecylenic acid.* (242° cor.). S.G. $\frac{0}{}$ ·9096. Formed by oxidation of the corresponding aldehyde (Borodin, *B.* 5, 481; Hell a. Schoop, *B.* 12, 193). Oil. Oxidised by chromic mixture to acetic and isovaleric acid (Gaess, *B.* 10, 455). The K salt is deliquescent. $CaA'_2\,\frac{1}{2}aq$: needles (from alcohol).

Decenoic acid $C_{10}H_{18}O_2$. *Decacrylic acid.* [86°]. S. (cold alcohol) ·08; (hot alcohol) 2. Occurs in cork. Amorphous. Acid to litmus (Siewert, *Z.* 1858, 383).

DECENOIC ALDEHYDE $C_{10}H_{18}O$. *Diisovaleric aldehyde.* (c. 189°). S.G. $\frac{0}{}$ ·861. Formed from isovaleric aldehyde by heating with zinc filings, or by treating with Na, KOH, K_2CO_3, or HCl (Borodin, *B.* 2, 552; 5, 481; 6, 983; Riban

Bl. [2] 18, 64; Kekulé, *B.* 3, 135; Gaess a. Hell, *B.* 8, 371). Oil. Does not combine with $NaHSO_3$. Reduces ammoanical $AgNO_3$.

DECENYL ALCOHOL $C_{10}H_{20}O$ *i.e.* CH_2:CH.CH_2.CPr_2.OH. *Allyl-di-propyl-carbinol.* (192° i.V.). S.G. $\frac{0}{0}$ ·8602; $\frac{24}{0}$ ·8427. C.E. (15°–29°) ·00101. H.C. 1,544,900 (Louguinine, *Bl.* [2] 35, 563). From di-propyl-ketone, zinc, and allyl iodide (Saytzeff, *A.* 196, 109). Oil, smelling like turpentine. Chromic mixture oxidises it to di-propyl-ketone, butyric acid, and propionic acid. Aqueous $KMnO_4$ gives CO_2H.CH_2.CPr_2.OH.

Acetyl derivative $C_{10}H_{19}OAc$. (210° i.V.). S.G. $\frac{0}{0}$ ·890; $\frac{21}{0}$ ·8733.

Decenyl alcohol $C_{10}H_{20}O$ *i.e.* CH_2:CH.CH_2.CPr_2.OH. *Allyl-di-isopropyl-carbinol.* (170°). S.G. $\frac{0}{0}$ ·8671; $\frac{24}{0}$ ·8477. C.E. (0°–24°) ·00095. From di-isopropyl-ketone, allyl iodide, and zinc (Lebedinsky, *J. pr.* [2] 23, 22). Oil, smelling like turpentine. $KMnO_4$ gives CO_2H.CH_2.CPr_2.OH and isobutyric acid. Forms a liquid dibromide.

Decenyl alcohol $C_{10}H_{20}O$. (c. 194°). From acetone (75 g.), allyl iodide (205 g.), isobutyl iodide (230 g.), and granulated zinc (Schatzky, *J. pr.* [2] 30, 216). Oil.

DECENYLENE *v.* DECINENE.

DECENYLENE TETRABROMIDE *v.* TETRA-BROMO-DECANE.

DECINENE $C_{10}H_{18}$. *Decenylene.* (c. 158°). S.G. $\frac{0}{0}$ ·787; $\frac{16}{0}$ ·774; $\frac{21}{0}$ ·770. R_∞ 77·1 to 78·8 (theory 75·8). Formed by heating allyl-di-propyl-carbinol (decenyl alcohol) with H_2SO_4 (1 pt.) and water (1 pt.) at 130°. The oily product is distilled, and the portion boiling at 150°–170° is distilled over sodium in an atmosphere of CO_2. Absorbs oxygen from the air. Combines with bromine forming $C_{10}H_{18}Br_4$. Oxidised by chromic mixture gives acetic, propionic and butyric acids (S. Reformatsky, *J. pr.* [2] 27, 389; *Bl.* [2] 40, 185).

Decinene $C_{10}H_{18}$. *Rutylene.* (150°). From diamylene bromide and alcoholic KOH (Bauer, *A.* 135, 344).

Decinene $C_{10}H_{18}$. *Sebacin.* [55°]. (above 300°). Formed by distilling calcium sebacate (Petersen, *A.* 103, 184).

Decinene $C_{10}H_{18}$. (165°). Formed by the action of alcoholic potash on di-bromo-decane derived from petroleum (Reboul a. Truchot, *A.* 144, 248).

Decinene $C_{10}H_{18}$. *Hydrocamphene.* [120°]. (160°). A product of the action of sodium on the solid hydrochloride $C_{10}H_{16}HCl$ derived from turpentine (Montgolfier, *A. Ch.* [5] 19, 145). Inactive.

Decinene $C_{10}H_{18}$. *Hydrocamphene.* [140° uncor.]. Prepared by the action of sodium and gaseous HCl on a benzene solution of bornyl chloride ($C_{10}H_{17}Cl$), or of camphor-dichloride ($C_{10}H_{16}Cl_2$) (Kachler a. Spitzer, *B.* 13, 615; *M.* 1, 589). White crystalline solid. V. sol. ether, less sol. alcohol and acetic acid. Does not combine with HCl. Very stable towards oxidising agents. Probably identical with the preceding.

Decinene (?)$C_{10}H_{18}$. *Camphine.* (c. 169°). S.G. ^{25} ·827. Formed by distilling camphor with iodine or HI (Claus, *J. pr.* 25, 264; Weyl, *B.* 1, 96). Br acts upon it by substitution.

DECINOIC ACID $C_{10}H_{16}O_2$. [52·5°]. (307°) Formed by the action of sodium on butyric ether (Brüggemann, *A.* 246, 132). Long needles.

DECINYL ALCOHOL $C_{10}H_{18}O$ *i.e.* $(CH_2{:}CH.CH_2)_2CPr.OH$. *Di-allyl-propyl-carbinol.* (194°). S.G. $\frac{0}{0}$ ·9707. C.E. (0°–20°). ·00082. R_∞ 78·7. From *n*-butyric ether, allyl iodide, and zinc; the product being poured into water and distilled (Saytzeff, *A.* 193, 362). Oil, smelling like turpentine.

Decinyl alcohol $C_{10}H_{18}O$ *i.e.* $(CH_2{:}CH.CH_2)_2CPr.OH$. *Di-allyl-isopropyl-carbinol.* (183° i.V.). S.G. $\frac{0}{0}$ ·8647; $\frac{20}{0}$ ·8512. From isobutyric ether, allyl iodide, and zinc (Riabinin a. Saytzeff, *A.* 197, 70; *Bl.* [2] 31, 199). Oxidised by the air.

Decinyl alcohol (?)$C_{10}H_{18}O$. (176°). From valerylene and diluted H_2SO_4 (Reboul, *A.* 143, 373). Oil.

Decinyl alcohol (?)$C_{10}H_{18}O$. (c. 211°). A product of the action of allyl iodide and zinc on acetic ether (Schestakoff, *J. pr.* [2] 30, 215).

DECIPPIUM. According to Delafontaine (*C. R.* 87, 632; 93, 63; *C. N.* 38, 223; 44, 67) *Samarskite* from North Carolina, and *Sipylite* from Virginia, contain an element belonging to the group of the earths, but differing from all the other metals of this class. To this element Delafontaine gave the name *Decippium.* The double sulphate of Dp and K is insoluble in saturated K_2SO_4Aq; on this fact is based a method of separating from terbium. Further researches are required before the existence of decippium can be regarded as established (*cf.* EARTHS; and EARTHS, METALS OF THE). M. M. P. M.

DECOIC ACID $C_{10}H_{20}O_2$. *Capric acid.* Mol.w. 172. [30°]. (269°). S.G. ^{37} ·930.

Occurrence.—1. As glyceryl ether in butter (Chevreul, *Recherches sur les corps gras*) and in cocoa-nut oil (Gorgey, *A.* 66, 295).—2. As iso-amyl ether in fusel oil from grapes (Fischer, *A.* 118, 307; Grimm, *A.* 157, 264), and in fusel oil from Scotch whiskey (Rowney, *A.* 79, 236).—3. In Limburg cheese (Iljenko, *A.* 55, 85).—4. To the extent of 5 p.c. in the fatty mass deposited by the water used to extract yolk (*suint*) from wool (Buisine, *C. R.* 105, 614).

Formation.—1. By the distillation of oleïc acid (Gottlieb, *A.* 57, 63).—2. By oxidation of oleïc acid by HNO_3 (Redtenbacher, *A.* 59, 54).—3. From octyl-aceto-acetic acid (Guthzeit, *A.* 204, 5).

Properties.—Slender needles, hardly sol. water, of faint rancid odour. Sol. alcohol and ether.

Salts.—AgA′. Needles from boiling water. Sl. sol. water.—BaA'_2. Plates from boiling water. Sl. sol. water, sol. alcohol.—CaA'_2.—MgA'_2.—CuA'_2.—NaA′. Sol. water.

Methyl ether MeA′. (224°).

Ethyl ether EtA′. (244°). S.G. ·862.

Iso-amyl ether (275°–290°). In fusel oil from grapes.

Chloride $C_{10}H_{19}OCl$. (c. 210°) (Grimm, *A.* 157, 272).

Amide $C_{10}H_{19}ONH_2$. [98°]. Prepared by digesting ammonic decoate at 230° under pressure; the yield is 75 p.c. (Hofmann, *B.* 15, 984).

DECOIC ALDEHYDE C_9H_{19}.COH (c. 106°) at 15 mm. Formed by distilling a mixture of barium decoate (caprate) and barium formate. Liquid. On reduction with zinc-dust and acetic acid it gives *n*-prim-decyl alcohol (Krafft, *B.* 16, 1716).

Isodecoic aldehyde $C_{10}H_{20}O$. (169° cor.). S.G. $^{\underline{0}}$ ·828. Formed by oxidation of iso-capryl alcohol. Oil. Does not combine with $NaHSO_3$ (Borodin, *J.* 1870, 680).

DECOMPOSITION, CHEMICAL. The breaking down of one definite kind of matter into simpler kinds is called chemical decomposition. By a definite kind of matter is meant, in chemistry, an element or a compound. The term decomposition can be applied in strictness only to one class of changes undergone by compounds. The products of the decomposition of a compound are either elements or compounds; the mass of each is different from the mass of the compound decomposed, and the properties of each are different from those of the original compound. The simplest cases of chemical decomposition are those brought about by the action of an external agency such as heat, light, or electricity on a compound; water, for instance, is decomposed by the electric current into hydrogen and oxygen; salammoniac is decomposed by heat into ammonia and hydrogen chloride. By a slight extension, the term chemical decomposition is used to include cases of chemical interaction between two or more bodies resulting in the formation of new bodies, some at least of which are simpler than the original substances. Thus when water and potassium interact potash and hydrogen are produced; the water is often said to be decomposed by the potassium, inasmuch as one of the products of the interaction is the element hydrogen, which was formerly combined with oxygen forming water. So when acetic acid and phosphorus pentachloride react to produce acetyl chloride, phosphorus oxychloride, and hydrochloric acid, each of the reacting bodies may be said to be decomposed by the other. This example shows that the term chemical decomposition is used as covering the greater number of reactions known as chemical changes. The combination of two elements, or of one element and compound, or of two (or more) compounds, would not generally be called a decomposition; nor would the term be customarily employed with reference to an isomeric or allotropic change, such as that of ammonium cyanate into urea, or of one form of crystalline arsenious oxide into the other form; but with these exceptions the terms chemical decomposition and chemical change have practically the same connotation.

When a chemical change between two or more bodies is called a decomposition, the term is generally used with the object of concentrating attention chiefly on one of the changing substances. Thus the change which occurs when potash solution reacts with chlorine to form potassium chloride and chlorate is a decomposition of the potash, but a combination of the chlorine with other elements. Again, when it is said that common salt is decomposed by sulphuric acid with production of hydrogen chloride, only one part of the chemical change is brought prominently forward; it might be necessary sometimes to say that sulphuric acid is decomposed by common salt with production of sodium sulphate; neither statement is a full account of the occurrence.

Among chemical decompositions, in a narrower sense of the term, processes of dissociation take a prominent place. In these processes one definite compound is resolved, by the action of heat, into two or more elements or compounds differing from itself, and each weighing less than the original compound; thus hydrogen iodide is dissociated into hydrogen and iodine, ammonium carbamate is dissociated into ammonia and carbon dioxide, and so on.

Chemical decompositions are special cases of chemical change; the laws which state the conditions and course of chemical changes apply to chemical decomposition. These laws are stated and discussed in other articles; *v.* especially AFFINITY, vol. i. p. 67; CHEMICAL CHANGE, vol. i. p. 731; COMBINATION, CHEMICAL, LAWS OF; COMPOSITION, CHEMICAL. M. M. P. M.

DECONENE $C_{10}H_{16}$. (c. 148°). From dibromo-decylene (rutylene bromide) and alcoholic potash (Bauer a. Verson, *A.* 151, 52; Tugolesoff, *J. R.* 13, 447). Oil, smelling like turpentine. Its bromide $C_{10}H_{16}Br_2$ gives no cymene when heated with aniline. HCl gives $(C_{10}H_{16})_2HCl$.

Isomerides *v.* TERPENES.

DECONOIC ACID $C_{10}H_{14}O_2$. *Tri-ethenyl-butyric acid* (?) (c. 255°). Formed by heating NaOEt and NaOAc in a current of CO at 205° (Geuther a. Fröhlich, *A.* 202, 309).

n-prim-**DECYL-ALCOHOL** $C_{10}H_{21}.OH$ *i.e.* $CH_3(CH_2)_8CH_2OH$. Mol. w. 158. [7°]. (119°) at 15 mm. S.G. (liquid) $\frac{7}{4}$ ·8389; $\frac{20}{4}$ ·8297; $\frac{99}{4}$ ·7734. Large rectangular prisms or a thick sweet-smelling highly-refractive liquid.

Formation.—Capric aldehyde (obtained by distilling barium caprate with barium formiate) is reduced with zinc-dust and acetic acid.

Acetyl derivative $C_{10}H_{21}OAc$ (125° at 15 mm.). Mobile peculiar-smelling liquid. Solidifies at a low temperature (Krafft, *B.* 16, 1716).

Decyl alcohol $C_6H_{13}CHPr.OH$. *Propyl-hexyl-carbinol.* (211°). S.G. $^{\underline{0}}$ ·839; $\frac{20}{0}$ ·826. From œnanthol and $ZnPr_2$ followed by water (Wagner, *Bl.* [2] 42, 330; *J. R.* 16, 329). Oil.

Decyl alcohol $C_{10}H_{21}OH$. (200°). S.G. $^{\underline{18.7}}$ ·858. From the decane of petroleum *viâ* decyl chloride (Lemoine, *Bl.* [2] 41, 165; *cf.* Pelouze a. Cahours, *J.* 1863, 529; *A. Ch.* [4] 1, 5).

Decyl alcohol $C_{10}H_{21}OH$. *Isocapric alcohol.* (203°). S.G. $^{\underline{0}}$ ·857. From isovaleric aldehyde and sodium (Borodin, *Z.* 1870, 415).

Acetyl derivative $C_{10}H_{21}OAc$. (220°). S.G. $^{\underline{0}}$ ·883.

Benzoyl derivative $C_{10}H_{21}OBz$. (above 280°).

Decyl alcohol $C_{10}H_{21}OH$. (c. 230°). S.G. ·84. From isoamyl isovalerate and sodium (Lourenço a. Aguiar, *Z.* 1870, 404).

Acetyl derivative $C_{10}H_{21}OAc$. (c. 232°).

Decyl alcohol $C_{10}H_{21}OH$. *Diisoamyl alcohol.* (203°). Formed, together with an isomeride (212°), from di-isoamyl (decane), by chlorination and displacement of Cl by OH (Grimshaw, *B.* 10, 1602).

DECYL BROMIDE $C_{10}H_{21}Br$. From di-isoamyl. Splits up on distillation into HBr and decylene.

DECYL CHLORIDE $C_{10}H_{21}Cl$. (200°). From di-isoamyl and Cl (Schorlemmer, *A.* 129, 246).

Decyl chloride $C_{10}H_{21}Cl$. (c. 202°) (Pelouze a. Cahours, *A. Ch.* [4] 1, 5). S.G. $\frac{19}{}$ ·908 (Lemoine, *Bl.* [2] 41, 165). From decane of petroleum and chlorine.

Decyl chloride $C_{10}H_{21}Cl$. (c. 195°) (Wurtz, *Bl.* [2] 5, 315). From Cl and the decane from di-bromo-decane (diamylene bromide).

Decyl chloride $C_{10}H_{21}Cl$. (c. 180°). From decyl alcohol (isocapryl alcohol) (Borodin, *J.* 1864, 338).

DECYLENE $C_{10}H_{20}$. *Di-amylene.* (156°–156·3°) at 757·4 mm.; S.G. $\frac{10}{4}$ ·7789; C.E. (10°–156°) ·00121; V.D. 4·86 (for 4·84); S.V. 211·3 (Schiff, *A.* 220, 90).

Formation.—1. From isoamyl alcohol by treatment with P_2O_5 or $ZnCl_2$ (Cahours, *A.* 30, 295; Balard, *A.* 52, 316).—2. From amylene (tri-methyl-ethylene) and $ZnCl_2$ or conc. H_2SO_4 (Bauer, *Sitz. W.* 44 [2] 87; Wyschnegradsky, *J. R.* 7, 165; Berthelot, *A.* 128, 311; Lebedeff, *J. R.* 7, 246; Erlenmeyer, *Z.* 1865, 362; Schneider, *A.* 157, 207).

Properties.—Oil. Yields, among the products of its oxidation, amethenic acid $C_7H_{14}O_2$.

Decylene $C_{10}H_{20}$. (163·7° cor.) at 744 mm. S.G. $\frac{20}{}$ ·7387. V.D. 70 (calc. 70). From di-isoamyl by treatment with Br and distillation of the resulting bromo-di-isoamyl (Lachowicz, *A.* 220, 178). Formed also by distilling decyl acetate (from decyl bromide and NaOAc). Aromatic liquid. Soluble in dilute H_2SO_4 (1:1). Combines readily with Br, but some HBr also comes off. The product is decomposed by distillation.

Decylene $C_{10}H_{20}$. (c. 159°). S.G. $\frac{14}{}$ ·855. From petroleum decane (Lemoine, *Bl.* [2] 41, 165).

Decylene $C_{10}H_{20}$. *Decanaphthene.* (161°). S.G. $\frac{0}{}$ ·795. R_∞ 77·2. Occurs in petroleum from Baku (Markownikoff a. Ogloblin, *J. R.* 15, 332).

Decylene $C_{10}H_{20}$. (171°). Among the products obtained by strongly heated paraffin (Thorpe a. Young, *A.* 165, 22).

Decylene $C_{10}H_{20}$. (175°). S.G. $\frac{0}{}$ ·791. From blubber by saponification and distillation of the lime salts of the resulting acids (Warren a. Storer, *Z.* 1868, 231).

Decylene $C_{10}H_{20}$. (176°). S.G. $\frac{0}{}$ ·823. From petroleum from Burmah (Warren a. Storer, *Z.* 1868, 231).

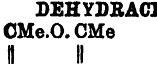
Isomerides *v. Tetrahydrides of* TERPENES.

DECYLENE GLYCOL *v.* DI-OXY-DECANE.

DECYLENE OXIDE $C_{10}H_{20}O$. *Diamylene oxide.* (170°–180°). From $C_{10}H_{20}(OAc)_2$ and solid KOH (Bauer, *Sitz. W.* 45 [2] 276). Oil. Reduces ammoniacal $AgNO_3$.

Decylene oxide $C_{10}H_{20}O$. (c. 201°). V.D. 5·3 (calc. 5·4). Formed by the action of conc. KOHAq on the product of the action of crude amylene on Bz_2O_2 at 110° (Lippmann, *M.* 5, 563). Does not reduce ammoniacal $AgNO_3$ nor combine with $NaHSO_3$.

DEHYDRACETIC ACID $C_8H_8O_4$ *i.e.*



$$\begin{array}{l}\text{CMe.O.CMe}\\ \|\qquad\quad \|\\ \text{CH.CO.C.CO}_2\text{H}\end{array}$$

(?). [109°]. (270° cor.). S. 1 at 0°.

Formation.—1. By passing the vapour of aceto-acetic ether through a glass tube filled with pumice and heated to redness (Geuther, *Z.* [2] 4, 655; Perkin, jun., *C. J.* 47, 240; 51, 489).—2. By the action of pyridine or picoline upon acetyl chloride; these bases probably only act by removing HCl, for they are found unaltered at the end of the reaction (Dennstedt a. Zimmermann, *B.* 19, 75).

Properties.—Needles or trimetric tables (from water). V. sol. hot water, hot alcohol, and ether. Fe_2Cl_6 colours its solution orange.

Reactions.—1. Boiling conc. NaOHAq splits it up into CO_2, acetic acid, and acetone. Alcoholic KOH forms, as intermediate products, aceto-acetic ether and acetic acid.—2. *Ammonia* forms oxy-di-methyl-pyridine (Perkin, *B.* 18, 682; Haitinger, *M.* 6, 105).—3. Zn and HCl forms an acid [187°] (Oppenheim a. Precht, *B.* 9, 1101).—4. PCl_5 forms $C_8H_6O_2Cl_2$ [101°], reconverted by water at 200° into dehydracetic acid.

Salts.—NaA′ 2aq.—BaA′$_2$ 2aq.—CaA′$_2$.—ZnA′$_2$ 2aq.—AgA′.

Methyl ether A′Me: [91°]; prisms; v. sol. water. Has distinct acid properties, forming $C_8H_6(Na)O_4Me$ (Perkin, *B.* 18, 218).

Ethyl ether EtA′. [92°].

Amide $C_8H_7O_3NH_2$. [209°]. From the acid and aqueous NH_3 (O. a. P.).

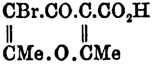
Anilide $C_8H_7O_3NHPh$. [115°].

Oxim $C_7H_8O_3C(NOH)$: [173°]; colourless crystals, sol. alcohol. Formed by the action of hydroxylamine on potassium dehydracetate. Fe_2Cl_6 gives a purple-red colouration.

Phenyl-hydrazide $C_7H_8O_3C(N.NHPh)$; [c. 207°]; glistening yellow tables (from alcohol). Formed by the action of phenyl-hydrazine on potassium dehydracetate (Perkin a. Bernhart, *B.* 17, 1522).

Chloro-dehydracetic acid $C_8H_7ClO_4$. [93°]. From dehydracetic acid and Cl (O. a. P.). Small needles.

Bromo-dehydracetic acid $C_8H_7BrO_4$ *i.e.*



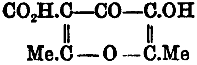
$$\begin{array}{l}\text{CBr.CO.C.CO}_2\text{H}\\ \|\qquad\quad \|\\ \text{CMe.O.CMe}\end{array}$$

(?). [137°].

Preparation.—Dehydracetic acid (5 g.) is dissolved in chloroform (50 g.), a slight excess of bromine and a little iodine are then added, and the whole warmed on the water-bath at about 50°. The reaction once started continues by itself and is finished in about 12 hrs. (Perkin, *C. J.* 51, 490).

Properties.—Plates and prisms. V. sol. hot alcohol, chloroform, benzene, and petroleum-ether, sl. sol. cold alcohol.

Oxy-dehydracetic acid $C_8H_8O_5$ *i.e.*



$$\begin{array}{l}\text{CO}_2\text{H.C—CO—C.OH}\\ \qquad\ \ \|\qquad\qquad \|\\ \quad\text{Me.C — O — C.Me}\end{array}$$

(?). [c. 253°].

Preparation. — Bromodehydracetic acid is dissolved in a little alcoholic potash, excess of the latter is then added, and the whole allowed to stand for several days at about 40° (Perkin, *C. J.* 51, 491).

Properties. — Four-sided crystals. M. sol. hot alcohol, almost insol. cold water, chloroform, petroleum-ether, benzene, and acetone. Is readily sol. alkalis. Sublimes with slight decomposition.

Salt.—$C_8H_6O_5Ag_2$ (?).

Acetyl derivative $C_8H_7O_4(OAc)$. [167°]. Rhomboidal plates. V. sol. hot alcohol, m. sol. benzene, chloroform, ether, and CS_2.

Isodehydracetic acid v. *Carbo-aceto-acetic ether*, vol. i. p. 20.

DEHYDRODIACETONAMINE v. Acetonamine.

DEHYDRACETONE-BENZIL v. Acetone-benzil.

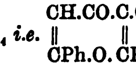
DEHYDRACETONE - PHENANTHRAQUINONE v. Acetone-phenanthraquinone.

DEHYDRACETOPHENONE-ACETO-ACETIC-ACID v. Acetophenone-aceto-acetic acid.

DEHYDRACETOPHENONE - ACETONE v. Acetophenone-acetone.

DEHYDRACETOPHENONE-BENZIL v. Acetophenone-benzil.

DEHYDRO-BENZOYL-ACETIC ACID



$$\begin{array}{l} CH.CO.C.CO_2H \\ \quad \| \qquad \| \\ CPh.O.CPh \end{array}$$

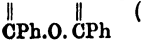
$C_{18}H_{12}O_4$ *i.e.* (?). [172°]. Prepared by heating benzoyl-acetic ether for 7 or 8 minutes at its boiling-point, alcohol being split off (Baeyer a. Perkin, jun., *B.* 17, 64; *C. J.* 47, 262; *Am.* 8, 101). Long yellow needles. V. sol. ether and chloroform, m. sol. alcohol, sl. sol. ligroïn.

Reactions.—1. By standing with cold alcoholic KOH it is reconverted into benzoyl-acetic acid.—2. It dissolves in cold H_2SO_4 with an olive-green colour, and on heating becomes a splendid violet, the spectrum of which exhibits the indigo bands; on dilution with water the colour vanishes.—3. *Sodium amalgam* reduces it to an acid $C_{18}H_{12}O_3$ [112°], and an acid $C_{18}H_{14}O_4$ [145°-150°].—4. Fe_2Cl_6 colours the hot alcoholic solution orange-red.—5. Does not combine with Br.—6. Does not react with Ac_2O. 7. Red-hot *soda-lime* gives acetophenone.—8. *Phenyl-hydrazine* forms a yellow compound. 9. PCl_5 gives $C_{18}H_{11}ClO_3$ [151°].

Salts.—$FeSO_4$ gives a blackish-violet amorphous pp., and Fe_2Cl_6 gives a deep scarlet pp. in neutral solutions (Baeyer a. Perkin, *B.* 17, 64). A'Ag: white flocculent pp.

Ethyl ether EtA'. [159°]. Needles. M. sol. alcohol, benzene, and CS_2, sl. sol. ether and light petroleum. Fe_2Cl_6 colours its alcoholic solution reddish-brown. NaOEt added to its ethereal solution forms a sodium derivative.

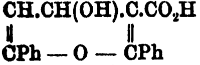
Derived acid $C_{18}H_{12}O_3$ *i.e.*



$$\begin{array}{l} C:CH.C.CO_2H \\ \| \qquad \| \\ CPh.O.CPh \end{array}$$

(?). [112°]. Formed as above (*Reaction* 3). Tables. V. sol. alcohol, ether, benzene, CS_2, and chloroform, almost insol. light petroleum. Does not decolourise Br in CS_2 solution. Conc. H_2SO_4 gives an intense orange solution which on warming becomes first colourless and then greenish-brown.

Derived acid $C_{18}H_{14}O_4$ *i.e.*



$$\begin{array}{l} CH.CH(OH).C.CO_2H \\ \| \qquad\qquad\quad \| \\ CPh - O - CPh \end{array}$$

(?). [145°-150°]. Found in the mother-liquor from which the above has separated. Yellow needles (from alcohol-petroleum). V. sol. most solvents, sl. sol. light petroleum and CS_2. Gives off CO_2 on fusion. The CS_2 solution does not decolourise Br in the cold; on warming HBr is given off. Conc. H_2SO_4 forms a yellow solution which becomes brownish-red on warming. Boiling Ac_2O forms $C_{20}H_{14}O_4$ [145°-150°] which crystallises from 80 p.c. acetic acid in yellow needles; it is v. sol. hot alcohol, benzene, and chloroform, but sl. sol. ether; and its alcoholic solution is turned scarlet by Fe_2Cl_6.

DEHYDROBENZYLIDENEDIACETOACETIC ETHER v. Benzylidene-diacetoacetic ether.

DEHYDRO-CHOLEÏC ACID v. Choleïc acid.

DEHYDRO-CHOLIC ACID v. Cholic acid.

DEHYDRO-CINCHENE v. Cinchene.

DEHYDRO-CINCHONINE v. Cinchonine.

DEHYDRO - CONQUININE v. Cinchona bases.

DEHYDRO-MUCIC ACID v. Mucic acid.

DEHYDRO-DIPROTOCATECHUIC ACID v. Tetra-oxy-di-phenyl di-carboxylic acid.

DELPHININE $C_{22}H_{35}NO_6$. [119°] (Blyth). S. ·02 at 20°; S. (alcohol) 5 at 20°; S. (ether) 9 at 20°; S. (chloroform) 6·3 at 20°. An alkaloid occurring in the seeds of stavesacre, or *Delphinium staphisagria* (Lassaigne a. Feneuille, *A. Ch.* 12, 358; Brandes, *Schw. J.* 25, 369; O. Henry, *J. Ph.* 18, 661; Couerbe, *A. Ch.* [2] 52, 352; *A.* 9, 101; Erdmann, *Ar. Ph.* [2] 117, 43; Marquis, *Russ. Zeit. Pharm.* 16, 449, 481, 513). Trimetric crystals (from ether); *a:b:c* = ·637:1: ·804. Decomposes at 120°. Inactive; has a slightly alkaline reaction. Tastes somewhat bitter. Conc. H_2SO_4 gradually forms a faintly brown solution changing to reddish-violet. A mixture of delphine (1 pt.) and malic acid (1 pt.) is coloured orange by H_2SO_4, the colour changing through deep rose to blue (Tattersall, *C. N.* 41, 63).

Salts.—B'2HCl.—$B'HAuCl_4$.—$B_3 2HNO_3$ (?). —$B'_3 2H_2SO_4$ (?).—$B'HHgI_3$.

Delphinoidine $C_{42}H_{68}N_2O_7$. [110°-120°] (?). S. ·017; S. (ether) 33. Separates from the ethereal solution out of which delphinine has crystallised (Marquis). Miscible with alcohol. Inactive. Tastes bitter. Has an alkaline reaction. With sugar and H_2SO_4 it becomes first brown, then green (*cf.* Schneider, *Fr.* 12, 219). H_2SO_4 and bromine water give a violet colour.

Salts.—B'2HCl. — $B'H_3Au_2Cl_7$. — $B'H_2SO_4$. —$B'2HNO_3$.—B'2HOAc.

Delphisine $C_{27}H_{46}N_2O_4$ (?). Once found in the mother-liquors, from which delphinine had separated. Less soluble than delphinoidine which it resembles.

Staphisagrine $C_{22}H_{33}NO_5$. [c. 90°]. S. ·5; S. (ether) ·117. Also occurs in stavesacre. Amorphous. Differs from the preceding alkaloids in being much less sol. ether. Soluble in all proportions in alcohol and chloroform. Optically inactive. Has an alkaline reaction. Conc. H_2SO_4 gives a cherry-red or violet colour. Does not give a green with sugar and H_2SO_4, or violet with H_2SO_4 and Br. HNO_3 colours it orange.

Salts. — B'HCl. — $B'HNO_3$. — B'HOAc. — $B'HAuCl_4$.—$B'HgI_2$ (?).—$B'_2H_2SO_4$.

DENSITIES, RELATIVE, of solids, liquids, and gases.—The subject of densities, absolute densities, relative densities, and specific gravities, deals with the following points:—

1. The mass contained in a definite volume of any one substance, or, knowing that weights are proportional to masses, the weights of definite volumes of different substances.

2. The ratio between the mass contained in any volume of a substance and the mass contained in an equal volume of a substance chosen as the standard, or, expressing this somewhat

differently, the ratio between the weight of a certain volume of any substance and the weight of an equal volume of the standard substance.

The terms in which these different ideas are embodied are *density*, *absolute density*, *relative density*, and *specific gravity*. Unfortunately there still exists a great deal of confusion as to the use of these terms, and even the standard text-books do not show agreement on this point. It is, therefore, necessary to give definitions of these terms showing the meanings which will be given to them in this article, and then to indicate wherein there is want of scientific precision in the ordinary use of the terms, and also wherein the meanings given to them in the text-books differ.

1. The *density*, or the *absolute density*, of any substance at any temperature is the mass of unit volume of that substance at that temperature.

Thus, if D_t stands for the absolute density of the substance at temperature t, M_t for the mass of the substance at temperature t, V_t for the volume of the substance at temperature t, we have the relation $D_t = \frac{M_t}{V_t}$; the numerical value for the absolute density will depend on the units of mass and length employed.

Making use of the notation of dimensional equations as introduced by Maxwell we get

$$[D] = \frac{[M]}{[V]} = \frac{[M]}{[L]^3} = [M]\,[L]^{-3};$$

that is, we find the unit of density to be of one dimension in mass, and of minus three dimensions in length.

2. The *specific gravity*, or the *relative density*, of a substance at any temperature is the ratio of the mass of any volume of the substance to that of an equal volume of some standard substance. The standard substance generally chosen is water at the temperature of its maximum density.

The above definitions show that relative density may be found by comparing the masses of any volume; we may choose the masses of unit volume, but inasmuch as we have given the name of *density* or of *absolute density* to the mass of unit volume, we shall thus get a new definition for specific gravity or relative density, namely,

The *specific gravity* or the *relative density* of a substance at any temperature is the ratio of its absolute density to the absolute density of the standard substance.

Putting S for the relative density, we get

$$S = \frac{D}{D_1} = \frac{\frac{M_1}{V_1}}{\frac{M_2}{V_2}}; \text{ and, if } V_1 = V_2, \text{ then } S = \frac{M_1}{M_2},$$

where M_1 and M_2 stand for the masses of volumes V_1 and V_2.

It is evident from the above formula that, inasmuch as S is the ratio between two masses, its value is independent of the unit chosen for mass. Hence the number expressing the relative density or specific gravity is a pure number, and has no dimensions.

On referring back to the two definitions given above, we find *density* and *absolute density*, *relative density* and *specific gravity*, used as synonymous terms. It does not matter which of them we employ, but it is better to make a definite choice at the outset and to abide by it. Absolute density goes with relative density, and density with specific gravity. The terms *absolute density* and *relative density* will be used in this article. Unfortunately the terms *density* and *specific gravity* are often used as synonymous, specific gravity being applied to solids and liquids and density to gases. To give the same meaning to two terms which express entirely distinct ideas is quite unpardonable. Attention has been drawn to this unscientific use of scientific terms in some of the more recent standard text-books, but there is still a difference of opinion as to the advisability of using the term specific gravity in preference to relative density, or *vice versâ*. Agreement on this point would be desirable.[1]

We have found that the numerical value for the absolute density depends on the system of units employed, while that of the relative density is the same whatever the system of units. If we use the C.G.S. system of units, as is now done in scientific work, we find that there is a definite relation between the unit of mass and the unit of volume, the unit of mass being the mass of unit volume of water at the temperature of its maximum absolute density. Therefore the maximum absolute density of water is equal to unity, and the relative density of any substance when referred to water at its maximum absolute density as standard is expressed by a number which is identical with that of its absolute density. Thus, taking the case of gold, its absolute density in the C.G.S. system of units is 19·2 grams, *i.e.* 1 c.c. of gold weighs 19·2 grams; the relative density of gold is also 19·2, that is, the mass contained in any volume of it is 19·2 times as great as that contained in an equal volume of water.

There are evidently two main methods for experimentally determining the relative density of any substance.

1. Determine its absolute density, that of the standard being known.

2. Determine the ratio of the mass of the substance to that of an equal volume of the standard.

A short account of the principles underlying the most important methods for determining relative densities is all that can be given here. For detailed accounts of the relative values of the various methods and for the necessary experimental precautions books on practical physics must be consulted. (The article *Dichte* in Ladenburg's *Handwörterbuch der Chemie*, 3, 231-280, is particularly complete.)

I. **Relative densities of solids.**—The standard substance is water at the temperature of its maximum density. It is not easy to produce this temperature and maintain it constant; however, we know accurately the density of water at various temperatures, so that we can always calculate what the mass of water at the temperature of the experiment would become at the temperature of maximum density.

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[1] The German equivalents of density (*Dichtigkeit*) and specific gravity (*Specifisches Gewicht*) are used in exactly the same sense as in English. There seems to exist a great deal of ambiguity about the use of the French terms *densité* and *poids spécifique*. The two are used as synonymous, or, if a difference is made, this consists in defining *densité* as the *mass* contained in unit volume, and *poids spécifique* as the *weight* of unit volume (*v.* Ditte, *Exposé de quelques propriétés générales des corps*).

1. *Experimental processes based on the first method*, that is, on determining the absolute density, that of water being known. — Using the C.G.S. system of units we find the absolute and the relative density to be numerically the same. From the formula $D = \frac{M}{V}$ we see that the experimental work consists in determining (*a*) a mass, that is practically a weight, (*b*) a volume. The following methods are used in practice.

(i.) The body is weighed in air and then thrown into a graduated vessel partly filled with liquid. The difference in readings before and after introduction of the solid gives its volume. The weight in grams divided by the volume in cubic centimetres gives the absolute density which is numerically equal to the relative density.

(ii.) By means of the *stereometer* or *volumenometer*. The use of this apparatus is based on the assumption of the truth of Boyle's law, according to which pressure × volume = constant, when temperature is constant. (For a description of the instrument reference must be made to a manual of practical physics.)

2. *Experimental processes based on the second method*, that is, on determining the ratio between the mass of the substance and the mass of an equal volume of the standard substance.

(i.) *The specific gravity bottle.*—The form and capacity of this instrument vary widely, according to the special purpose for which it is used. Generally it is a small flask of thin glass which will hold a definite volume of liquid. The amount of liquid is adjusted either by filling the flask up to a mark on the neck or by filling it completely and inserting a perforated stopper through which excess of liquid flows out. The observations necessary are :

(*a*) The weight of the flask filled with distilled water $W_{,}$.

(*b*) The weight of the solid in air W.

(*c*) The weight of the flask into which the solid has been introduced filled with water up to the mark or completely as before $W_{,,}$.

Then we know that owing to the introduction of the solid into the flask a volume of water has been expelled which is equal to that of the solid introduced, the weight of this volume of water is $(W_{,}+W)-W_{,,}$, therefore the relative density of the solid is

$$S = \frac{\text{weight of solid}}{\text{weight of equal volume of water}}$$

$$= \frac{W}{W_{,}+W-W_{,,}}.$$

The following methods for determining relative densities of solids are based on the principle of Archimedes, according to which a body when immersed in a liquid experiences a loss of weight equal to the weight of the volume of liquid displaced.

(ii.) *The hydrostatic balance.*—The solid is weighed in air; call this weight W; it is then suspended by means of a fine thread from one of the scale pans and weighed again; call this $W_{,}$; it is then suspended as before, immersed in water and weighed; call this $W_{,,}$. Then, by the principle enunciated above, the weight of water displaced by the solid—that is, the weight of a volume of water equal to the volume of the solid immersed—is $W_{,,}-W_{,}$, and the relative density of the solid is $S = \frac{W}{W_{,,}-W_{,}}$.

(iii.) *Jolly's balance.*—The principle is the same as that of the hydrostatic balance.

(iv.) *Nicholson's hydrometer.*—This instrument belongs to the class of hydrometers in which the volume immersed is kept constant while the weight is changed. It consists of two cups connected by a fine stem on which is placed the mark of constant immersion. The instrument is placed in a vessel of distilled water of suitable size and the following observations are made :—

(*a*) Weights, W, are placed in the upper cup till the instrument sinks to the mark.

(*b*) The solid, together with sufficient weights, $W_{,}$, to produce the same result, are placed in the upper cup.

(*c*) The solid is placed in the lower cup, and weights, $W_{,,}$, in the upper cup till the instrument sinks to the mark again. From these data we find the relative density $S = \frac{W-W_{,}}{W_{,}-W_{,,}}$.

All the methods mentioned must be modified for

1. Porous substances. In order to determine what is termed the *apparent density*, that is, the weight of the apparent volume including air spaces, porous substances pervious to water must be covered with varnish before immersion.

2. Substances soluble in water. It is necessary to substitute for water some liquid of known relative density, $\rho_{,}$, in which the solid will not dissolve. Then if ρ is the relative density of the solid when referred to the liquid of density $\rho_{,}$ as standard, its relative density referred to water is $\rho \cdot \rho_{,}$.

3. Solids lighter than water. (*a*) A liquid of known density in which the solid will sink is substituted for water. The calculation is the same as above in 2. (*b*) The solid may be attached to one of known weight, *w*, and known relative density, $\rho_{,}$, and of such a volume that the two together will sink. The heavy solid is called a *sinker*; the form it takes must vary according to the light solid, the relative density of which is required. The calculation is simple. Let the weight of the solid in air be W; the total loss of weight on immersing sinker plus solid $= W_{,}$; then weight of water displaced by sinker $= \frac{w}{\rho_{,}}$, therefore, loss of weight on immersion due to light solid $= W_{,} - \frac{w}{\rho_{,}}$,

and relative density of light solid $= S = \frac{W}{W_{,}-\frac{w}{\rho_{,}}}$.

(*c*) The solid may be prevented mechanically from rising; this might be done by having a wire cage attached to the lower pans in a Jolly's balance or in a Nicholson's hydrometer.

II. Relative densities of liquids.—The standard is water at the temperature of its maximum density.

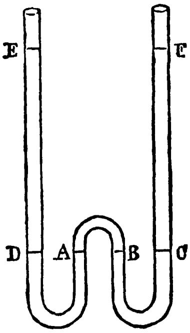
1. *Experimental processes based on the determination of the absolute density* are not numerous. Specific gravity bottles which when filled up to a mark in the neck contain a definite volume, generally marked outside, are much in use. The difference between the weight of the bottle when filled with liquid and when empty gives the weight of a known volume of liquid, from which the absolute density, *i.e.* the weight of unit volume, can be calculated.

2. *Experimental processes based on determining the ratio between a specified mass of the liquid and that of an equal volume of water.*

(i.) *The hydrostatic balance.*—A glass rod is weighed first in air, then immersed in the liquid, and finally immersed in water. If W and $W_{,}$ are the losses of weight on immersion in the liquid and in water respectively, then these are the weights of equal volumes, as both are the weight of a volume of liquid equal to the volume of the rod. Hence the relative density of the liquid is $S = \frac{W}{W_{,}}$.

(ii.) *The specific gravity bottle.* — A glass vessel of suitable size and form is weighed when empty in air—let this be W; it is then weighed when filled with water—let this be $W_{,}$; it is again weighed when filled with the liquid—let this be $W_{,,}$; the relative density is given by the formula $S = \frac{W_{,,} - W}{W_{,} - W}$.

(iii.) Method based on the fact that when *two columns of liquid are in equilibrium with each other their heights are inversely proportional to their densities.*—A tube of the shape



shown in the figure is very suitable. There is air between A and B, water between B and F, and the liquid under examination between A and E. The vertical distances A E and B F are measured—let these be h and h′; then $\rho h = \rho_{,} h_{,}$ where ρ and $\rho_{,}$ are the absolute densities of the two liquids, but $\rho_{,} = 1$ and $\rho = \frac{h_{,}}{h}$.

(iv.) *Hydrometers.*—These are of various kinds.

A. The volume immersed is kept constant, and is indicated by a mark on the stem. The relative density is given by $S = \frac{G + W}{G + W_{,}}$, where G is the weight of the hydrometer, W is the weight necessary to make it sink to the mark when immersed in the liquid, and $W_{,}$ is the weight required to cause it to sink to the same mark when immersed in water. Nicholson's and Fahrenheit's hydrometers belong to this class.

B. The weight of the hydrometer is kept constant, and the volume immersed varies. A scale is attached to the stem; this is divided differently in different types of instruments.

a. It is divided into equal parts; to find the relative density it is necessary to consult a table in which these arbitrary units are expressed in terms of densities. Beaumé's hydrometer is an instrument belonging to this class.

β. The scale-readings give directly the relative densities sought. In order that this may be done the volumes immersed must decrease in harmonical progression as the densities increase in arithmetical progression. Twaddle's hydrometer belongs to this class. A difference in relative density of 0·005 is taken as one degree, so that there are 200° for a range of relative density between 1 and 2. Hence for a reading of *n* Twaddle, the relative density $S = 1 + \frac{n}{200}$.

(v.) *Specific gravity balls.*—These are sets of small glass balls with the number indicating a relative density marked on each. The experimental work consists in ascertaining which ball will just float in the liquid. The number on the ball gives directly the relative density of the liquid.

The nature of the liquid, the quantity of it at our disposal, and the degree of accuracy required, must decide to which of the above methods the preference is to be given. For very rapid and only approximate work it is best to use a hydrometer, while the specific gravity bottle, which can be made very small and so as to present a minute surface for evaporation, is best for accurate work as well as for cases in which we have to deal with only a small quantity of liquid or with a very volatile liquid.

III. Relative densities of gases and vapours.—The standard is air at 0° and a pressure of 760 mm. Relative densities are found by determining the absolute density at a known temperature and pressure, and then calculating what that density would be at 0° and 760 mm. pressure, on the assumption of the rigorous truth of Boyle's and Charles's laws. The absolute density of the standard, that is of air, is supposed known; Regnault's value, 0·001293, is generally accepted. It is to be regretted that the word *density* is almost universally used when the *relative density* or the *specific gravity* of a gas or vapour is meant.

A. *Relative densities of gases*, that is, of substances which are gaseous at the ordinary temperature.

1. *Regnault's method.*—The method first used by Biot a. Arago[1] was wonderfully improved by Regnault.[2] A large glass balloon is

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[1] Biot a. Arago, 'Détermination du poids du litre d'air,' *Mémoires de l'Acad.* 1806.

[2] Regnault, 'Détermination de la densité des gaz,' *Mémoires de l'Institut*, XXI.

filled with the gas at pressure H, and the temperature of melting ice. In order to avoid the very uncertain correction for buoyancy in air, which is of the greatest importance in weighing quantities of gas, which are often lighter than the air displaced, the balloon is weighed when counterbalanced by one of the same volume and made of the same glass. It is then exhausted to pressure h, the temperature being kept at zero, and weighed again. The difference, W, between the two weights gives the weight of the gas filling the balloon at pressure H-h, from which that at normal pressure is deduced to be $=W_0=W.\frac{760}{H\text{-}h}$. The volume of the balloon being known or determined, we possess all the necessary data for calculating the absolute density of the gas. The utmost has been done from the physical side to secure accuracy in these determinations; the great difficulty at present is to obtain the gases used in a state of sufficient chemical purity.

2. *Bunsen's method.*[1]—This is based on the law that the velocity of effusion of gases through fine tubes is inversely proportional to the square roots of their relative densities. This method is applicable when only small quantities of gases are at our disposal, and when only approximate values are required.

B. *Relative densities of vapours*, that is, of substances which must be raised to a temperature above that of the atmosphere, in order to change them into gases.

Here, again, it is the absolute density which is determined directly, and which is referred to that of air. The experimental processes consist either in determining the weight of a known volume of gas (Dumas's method), or in determining the volume occupied by a known weight[2] (Gay-Lussac's, Hofmann's, Meyer's method).

Let W be the weight of any volume, v, of any vapour at temperature t and pressure p; let W′ be the weight of an equal volume of air at the same temperature and pressure; then the relative density of the vapour $d=\frac{W}{W_{,}}$ but

$$W_{,}=v\delta.\frac{1}{1+\alpha t}\cdot\frac{p}{760}\therefore d=\frac{W}{v\delta}\cdot\frac{760}{p}(1+\alpha t)$$

where δ is the weight of 1 c.c. of air at 0° and 760 mm. According to this formula, in which δ and α are constants, four magnitudes, v, t, p, and W, must be determined in order to give us d.

Dumas's method.—The weight w of a thin glass balloon ending in a long fine neck, when full of dry air at temperature T and pressure P, is determined. Excess of the substance to be vapourised is introduced into the balloon, which is then heated in a bath to a suitable temperature. When vapour ceases to escape from the neck of the balloon, the end of the neck is sealed by melting in the blowpipe; the temperature, t, of the bath, and the atmospheric pressure, p, being noted. The weight, $w_{,}$, of the balloon full of vapour is thus determined. By breaking the point of the neck under water or mercury, the balloon is completely filled with one of these liquids, and the difference between the weight of it when filled and when empty gives the weight of liquid filling it; the absolute density of this liquid being known, we have the data required for calculating the volume of the balloon. We have now obtained v, t, and p by direct observations. We must find the weight, W, of vapour filling the balloon at temp. t, and pressure p.

$W=w_{,}-$weight of glass

$=w_{,}-(w-$air filling balloon at temp. T and pressure P)

$=w_{,}-w+w_{,,}$

where $w_{,,}=v\delta.\frac{1}{1+\alpha T}\cdot\frac{P}{760}$.

Gay-Lussac's method.—A tube of about half the barometric height, divided into cubic centimetres, and completely filled with mercury, dips into a trough of mercury and is surrounded by a vessel of water. The whole apparatus can be heated to the required temperature. A known weight of the substance contained in a small glass bulb is allowed to rise in the tube filled with mercury. On heating the apparatus the bulb breaks, and the substance is changed to vapour. The four data necessary for substitution in the above formula are obtained in the following way:—

W = the weight of substance, is obtained by direct weighing;

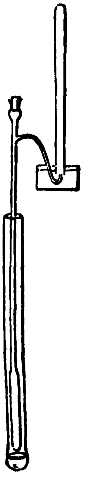
v = the volume, is obtained by reading the volume occupied by the vapour in the tube in terms of scale-divisions;

t = the temperature of the surrounding water;

p is given by the difference (reduced to 0°) between the height of the barometer and the height of the mercury column in the tube.

Hofmann's method.—This method is a modification of that of Gay-Lussac, a tube longer than the barometric height being used. The observations and calculations are the same as in Gay-Lussac's method. This method has the advantage that the substances are volatilised at temperatures lower than their ordinary boiling-points.

V. Meyer's method.—A known weight, W, of substance is dropped into a glass vessel of the form shown in the figure. The bulb of the apparatus is kept at a temperature higher than the boiling-point of the substance. The volume, v, of the air which escapes through the side tube, and whose place in the tube is taken by an equal volume of vapour, is collected and measured at temp. t and pressure p. We have so obtained all the data necessary. This method is very rapid, and it possesses the additional advantage of not requiring a determination of the temperature of the vapour itself, a process which is always attended with great uncertainties.



Corrections to be applied in determinations of relative densities. The relative density being the ratio of two absolute densities, we have to consider the circumstances which produce a change in the absolute density, and how we can introduce suitable corrections. The absolute density being got by dividing the weight by the volume, it is best to consider the corrections to be applied to each of these two quantities separately.

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[1] Bunsen, *Gasometrische Methoden.*

[2] *Cf.* ANALYSIS, vol. i. pp. 227-229.

1. *The weight.*—In order to eliminate errors due to the balance we must in all accurate work use the method of double weighing. This gives the true weight in air; the true weight *in vacuo* is given approximately by

$W = w\left(1 - \frac{\lambda}{\rho} + \frac{\lambda}{\sigma}\right)$, where w = true weight in air.

λ = relative density of air at the moment of weighing. This will depend on, and entail a knowledge of, the temperature, pressure, and hygroscopic condition, of the air.

σ = relative density of substance weighed. The approximate value for this obtained by using the uncorrected weight may be used.

ρ = relative density of the weights.

2. *The volume.*—The volume changes with the temperature and with the pressure.

a. Influence of temperature.—In nearly all cases the volume increases as the temperature is raised. Hence the absolute density, which varies inversely as the volume, decreases. If the volume V_0 at temperature 0° changes to V_t at temperature t, where $V_t = V(1+t\alpha)$, α being the coefficient of cubical expansion, the density D_0 changes to $\frac{D_0}{1+t\alpha}$.

It is therefore necessary in all accurate density determinations to state the exact temperature at the time of the experiment, and to record the result as relative density at temperature t', or if the determination has to be reduced to normal temperature, that is, to the temperature of the standard (4° when water, 0° when air), it is necessary to calculate what the absolute density at that temperature would be from the above formula, knowing the value for α.

b. Influence of pressure.—The change in volume owing to change in atmospheric pressure is imperceptible in the case of liquids and solids, but it is very large in the case of gases and vapours. Boyle's law gives us the means of calculating what the volume would be at normal pressure, that at any other pressure being known. The volume being inversely proportional to the pressure, the absolute density is directly proportional to the pressure.

Lord Rayleigh has pointed out (*Pr.* 43, 356) that the glass balloon used in Regnault's method for determining the relative densities of gases when exhausted is sensibly compressed by the pressure of the air; hence the *tare* of the balloon is too large because of the lessened buoyancy of the atmosphere, and therefore the weight of the gas when the balloon is filled is too small. A correction must therefore be experimentally made for each balloon used (for method *v.* Lord Rayleigh *l.c.*, also Cooke and Richards, *P. Am. A.* 24, 184).[1]

It remains now to indicate in how far the determination of the density, that is, of one of the physical constants, of various kinds of matter is of importance in those investigations into the constitution and the decompositions of matter with which the chemist is concerned. In these investigations it is often found more convenient to deal with the reciprocal of the density $\frac{1}{d}$ to which the name of *specific volume* has been given.

Let us first consider those cases in which we are concerned only with the constitution of substances in the state of chemical equilibrium, and not with chemical change.

1. The density being a well-defined physical constant, a determination of its value tells us in many cases whether the substance under examination is or is not approximately pure. It must, however, be borne in mind that in the case of many metallic elements the value of the relative density will depend on the previous treatment the substance has undergone, such as whether it has been hammered or drawn into wire, whether it has been tempered, &c.

2. Many tables have been compiled, in which the percentage of acid or of alkali contained in an aqueous solution of definite relative density is given. By the help of such tables the determination of the relative density enables us at once to estimate quantitatively the acid or alkali present in a known volume of the solution.

3. How the determination of the relative density of a gas or of a vapour gives us the means of calculating its molecular weight will be found described in the article **Atomic and molecular weights** (vol. i. p. 336).

4. Those elements which exist in allotropic modifications, and those compounds which show polymorphism, differ, though often only slightly, in density. Thus we have

Sulphur		*Phosphorus*	
Octahedral	2·05	White . .	1·82
Prismatic	1·98	Red . .	2·2
Amorphous insoluble	1·95		

Carbon		*Arsenious oxide*	
Diamond	3·55	Amorphous vitreous	3·7385
Graphite	2·3	Octahedral	3·695
Gas carbon	1·885	Rhombic .	3·85

Titanic acid		*Calcium carbonate*	
Rutile	4·24	Arragonite	2·94
Brookite	4·15	Calcite .	2·72
Anatase	3·9		

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[1] Dumas' method for determining the relative densities of gases is described in *A. Ch.* [2] 33, 337; Gay-Lussac's in Biot's *Traité de Phys.* 1, 291; Hofmann's in *B.* 1, 198; and Victor Meyer's in *B.* 11, 1868 and 2253. For criticisms on, and modifications of, Meyer's method *v. B.* 12, 609, and 1112; 13, 401, 851, 991, 1079, 1185, and 2019; 14, 1727; and 15, 137, 1161, and 2775 (in the last paper by V. Meyer (*B.* 15, 2775) will be found an interesting and valuable criticism of the various methods for finding the rel. densities of gases); *v.* also *B.* 16, 1051; 19, 1861; also *C. J. Trans.* for 1880, 491. Modifications of Dumas's method are described by Bunsen, *v. Gasometrische Methoden*, 2nd ed. 1877, p. 172; also by Pettersson and Ekstrand, *B.* 13, 1191; and especially by Pawlewski, *B.* 16, 1293. Thorpe (*C. J. Trans.* for 1880, 147–150) has described a very complete method based on Hofmann's process. V. Meyer (*B.* 9, 1260, and 10, 2068) has described a method based on the displacement of mercury. In *W. A.* 22, 465 and 493, von Klobukow describes two processes for determining vapour densities with great accuracy; one is adapted for bodies with low boiling-points, the other for bodies which boil at high temperatures. La Coste (*B.* 18, 2122) describes a modification of V. Meyer's apparatus whereby the vapour densities of easily decomposable compounds may be determined at low temperatures and under very small pressures. A modification of V. Meyer's apparatus, by which a vapour density and the exact temperature of observation can be simultaneously determined, is described by Nilson and Pettersson in *J. pr.* [2] 33, 1; *v.* also Schall, *B.* 20, 1433. Malfatti and Schoop (*Z. P. C.* 1, 159) describe an apparatus for determining vapour densities under small pressures.

Silica

Quartz . . . 2·65
Tridymite . . 2·3

(*cf.* Allotropy, vol. i. p. 128). Little has been done as yet in tracing the connexions between these differences in density and the other physical and chemical properties of these substances, but some interesting facts have been brought to light. Thus we know that long-continued heating changes the relative density of *anatase*, 3·9, and of *brookite*, 4·15, to 4·24, which is the relative density of *rutile*; in the case of silica, and in that of calcium carbonate, the relative density of the heavier variety is changed into that of the lighter variety, by the action of heat. It has also been noticed that in a great many cases the higher relative density belongs to that allotropic modification which contains the less potential energy in so far as there has been production of heat in the change from the less dense to the more dense modification. Thus 80 gram units of heat are produced in the change of 32 grams of prismatic sulphur (rel. dens. 1·98) into octahedral sulphur (rel. dens. 2·05); the change of white phosphorus (rel. dens. 1·82) to red phosphorus (rel. dens. 2·2) is accompanied by the production of about 25,000 thermal units per 31 grams phosphorus changed. However, the case of the change of *arragonite* (rel. dens. 2·94) to *calcite* (rel. dens. 2·72), which is accompanied by the production of 4,000 heat units per 100 grams material changed, as well as other similar cases, prove that this rule is by no means general.[1]

5. It has been observed that on bringing together quantities a and a' of two substances of relative density d and d', the resulting density is not given by $\Delta = \frac{a+a'}{\frac{a}{d}+\frac{a'}{d'}}$; that is the resulting volume is not the sum of the volumes of the constituents. The following cases have been investigated:—

I. *Solution of a salt in water.*—Contraction generally takes place. From measurements of the amount of contraction, and of the specific heat of the solution, and the coefficient of expansion, Deville has calculated the amount of heat due to the contraction, and has tried to show that in most cases this is sufficient to account for all the thermal phenomena of solution.

It has been observed further that the amount of contraction increases with the quantity of the solvent, approaching a maximum. Also the amount of contraction for the same amount of solvent decreases as the temperature at which solution is effected is raised. The most interesting researches in connexion with this subject are those of Valson,[2] who has endeavoured to show that the contraction produced on dissolving a salt in water is made up of two parts, one of which is a characteristic constant of the basic radicle, and the other is a characteristic constant of the acidic radicle.

II. *Mixture of two liquids.*—A contraction always takes place which varies in magnitude with the relative quantities of the two liquids used. Here again Deville has tried to explain the thermal effect produced on mixing the two liquids by means of this contraction. The volume-change on mixing alcohol and water is the one which has been most thoroughly studied.

III. *Chemical action between two solutions.*—The cases studied deal mainly with neutralisation-phenomena. It has been established that the volume-change is expansion if the bases are KOH and NaOH, and contraction if the base is $NH_4.OH$. Here also the volume-change decreases as the temperature is raised. Ostwald, who investigated the density changes attendant on the neutralisation of dilute aqueous solutions, has arrived at a law the same as that found by Valson for solution. He found the volume-change due to chemical change to be the sum of two constants which belong individually to each of the components, and which do not depend on the substance with which each component combines.

6. A knowledge of the relative density of an element or of a compound is necessary for the determination of the constants;

$$\textit{atomic volume} = \left(\frac{\text{atomic weight}}{\text{relative density}}\right)$$

$$\text{and } \textit{molecular volume} = \left(\frac{\text{molecular weight}}{\text{relative density}}\right).$$

A description of how the atomic volume, regarded as a periodic function of the atomic weight, assists in classifying the elements will be found in the articles Classification, chemical, and Periodic law. The generalisations arrived at with regard to molecular volumes of solids, and especially of liquids, will be dealt with in the article, Specific volumes, in vol. iv.

7. Another physical constant which entails a knowledge of the relative density of a body, and which has led to some valuable generalisations as to the interdependence of chemical constitution and physical properties, is the *refraction equivalent*. This constant is defined as $\frac{\mu-1}{d}M$, where μ is the refractive index, M the molecular weight, and d the relative density, of the substance under examination. On this subject *v.* Physical methods used in chemistry.

The cases in which a knowledge of the relative density has been employed in the solution of problems belonging to chemical kinetics are but few.

1. The change in the relative density of vapours and gases (calculated to normal temperature and pressure) under different temperatures and pressures has been utilised to trace the rate of decomposition relatively to the change of temperature or pressure (*v.* Dissociation).

2. From a knowledge of the volume-change produced on neutralising a base A by an acid B, and on neutralising A by another acid C, as well as from knowing the specific volume of a solution containing A, B, and C, in equivalent quantities, Ostwald deduced the chemical composition of this solution, that is, he determined the ratio between the quantities present of AB and AC. The knowledge of this ratio enabled him to calculate the coefficients of relative affinity of the acids B and C (*v.* Affinity, vol. i. p. 75).

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[1] St. Claire Deville, *Sur la Contraction et la Chaleur de Contraction* (*C. R.* 50).

[2] Valson, *Propriétés modulaires des solutions salines au point de vue des densités* (*C. R.* 63).

3. In his researches on the velocity of chemical change as dependent on the varying conditions of the experiment, van 't Hoff[1] investigated the velocity of the change of rhombic sulphur into monosymmetric by observing the increase in volume at fixed intervals of time. The increase in volume being due to the change of rhombohedral sulphur of relative density 2·05 into oblique sulphur of relative density 1·98. I. F.

DEOXIDATION. This term was originally used to denote any process wherein oxygen was removed, wholly or in part, from a compound. Thus the formation of $KClO_3$ by heating $KClO_4$, as well as that of KCl by heating $KClO_3$, are alike deoxidations; similarly the production of Cr_2O_3 from CrO_3 by the action of alcohol, and the formation of Cr by heating Cr_2O_3 with carbon, are deoxidations. But as the term *oxidation* (*q. v.*) has been widened to include those chemical reactions wherein the negative or acidic radicle of a compound is increased relatively to the rest of the body, and also those wherein an element combines with a more negative element, or with a radicle more negative than itself, so has the term deoxidation been extended until it is now generally applied to all processes which result in the withdrawal of the whole or a part of the negative radicle of a compound.

The terms *deoxidation* and *reduction* are practically synonymous; the latter is more commonly used than the former.

As thus employed the terms deoxidation and oxidation are correlative; the deoxidation of one body is accompanied by the oxidation of another. Thus, to take a very simple case, when hydrogen is burnt in oxygen with production of water, the hydrogen is oxidised and the oxygen may be said to be deoxidised. If the reaction is represented in molecular formulæ the processes of oxidation and deoxidation are made apparent; $2HH + OO = 2H_2O$. Similarly, when hydrogen and chlorine combine, $HH + ClCl = 2HCl$, the hydrogen is oxidised while the chlorine is deoxidised or reduced.

Any element or compound which reacts with several classes of compounds to produce less oxidised bodies is called a *deoxidising agent* or *reducing agent*; while any element or compound which generally reacts to form bodies more oxidised than the original substances is called an *oxidising agent* or *oxidiser*. Probably every element and compound takes part in some chemical changes in which it acts either as an oxidiser or a deoxidiser; but these terms are generally confined to such elements and compounds as frequently react in the way indicated by the names. The following equations exhibit some common cases of deoxidation:—

Original element or compound		Deoxidiser		Deoxidised product		Oxidised product
O_2	+	$2H_2$	=	$2H_2O$	+	$(2H_2O)$
(in this case the water may be regarded as produced either by the oxidation of hydrogen or by the reduction of oxygen)						
Cl_2	+	H_2	=	$2HCl$	+	$(2HCl)$
O_3	+	Hg	=	O_2	+	HgO
(in this case the ozone is reduced to oxygen)						
$2Cl_2$	+	$2HgO$	=	Hg_2OCl_2	+	Cl_2O
Cl_2	+	K_4FeCy_6	=	KCl	+	K_3FeCy_6
$2HNO_3$	+	Sn	=	N_2O_3	+	$SnO_2 + H_2O$
$2KClO_3$	+	$3C$	=	$2KCl$	+	$3CO_2$
Fe_2O_3	+	$3H_2$	=	$2Fe$	+	$3H_2O$
CuO	+	CO	=	Cu	+	CO_2
$BeCl_2$	+	Na	=	Be	+	$2NaCl$
$Fe_2(SO_4)_3Aq$	+	SO_2	=	$2FeSO_4Aq$	+	$2SO_3Aq$
$2FeCl_3Aq$	+	Zn	=	$2FeCl_2Aq$	+	$ZnCl_2Aq$
H_2O_2Aq	+	HNO_2Aq	=	H_2O	+	HNO_3Aq
$2HgCl_2Aq$	+	$SnCl_2Aq$	=	$2HgCl$	+	$SnCl_4Aq$
$HgCl_2Aq$	+	$SnCl_2Aq$	=	Hg	+	$SnCl_4Aq$
$2AgNO_3Aq + H_2O$	+	C_2H_4O	=	$2Ag$	+	$C_2H_4O_2 + 2HNO_3Aq$
$K_2Mn_2O_8Aq$	+	$3H_2C_2O_4Aq$	=	$K_2OAq + 2MnO_2$	+	$3H_2O + 6CO_2$
$FeCl_3Aq$	+	$KIAq$	=	$FeCl_2Aq + I$	+	$KClAq$

Among the substances commonly used in the laboratory to accomplish deoxidations, hydrogen, carbon, carbon monoxide, sulphur dioxide, nitrous acid or a nitrite, stannous chloride, and aldehyde are prominent. The conditions under which deoxidations occur vary much: thus, $HgCl_2Aq$ is almost instantly reduced by $SnCl_2$ at the ordinary temperature; to reduce $Fe_2(SO_4)_3Aq$ completely to $FeSO_4$ by SO_2 the gas must be passed into the liquid for a long time, even when the liquid is kept hot; $K_2Mn_2O_8Aq$ is reduced by $H_2C_2O_4Aq$ rapidly if the liquid is warm and contains sufficient H_2SO_4 to dissolve the MnO_2 produced; to effect the complete reduction of $FeCl_3Aq$ by KI the iquid must be slightly acid, and the reaction should proceed for some time at a fairly high temperature and under increased pressure; Fe_2O_3 is deoxidised by H when a stream of the gas is passed over the heated oxide; to reduce $BeCl_2$ by Na the chloride must be kept molten (*cf.* articles COMBUSTION, OXIDATION, REDUCTION). M. M. P. M.

DEOXY- *v.* DESOXY-.

DEOXYBENZOÏN *v.* PHENYL BENZYL KETONE.

DEOXY-BENZOÏN-ACETIC ACID *v.* PHENYL-BENZOYL-PROPIONIC ACID.

DEOXY-BENZOÏN CARBOXYLIC ACID *v.* PHENYL BENZYL KETONE CARBOXYLIC ACID.

Anhydride *v.* BENZYLIDENE-PHTHALIDE.

DESMOTROPY. A term given to the breaking up of the 'double bonds' in the benzene ring. Thus phloroglucin forms a penta-ethyl derivative in which the five ethyl groups are directly united to ring carbon atoms. The constitution of this body, according to Herzig a. Zeisel (*M.* 9, 217), must be

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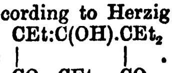
[1] *Études de Dynamique Chimique.*



$$\begin{array}{l}\mathrm{CEt{:}C(OH).CEt_2}\\ |\qquad\qquad\quad |\\ \mathrm{CO\,.\,CEt_2\,.\,CO}\end{array}.$$

DESOXALIC ACID $C_5H_6O_8$ *i.e.* $CO_2H.CH(OH).C(OH)(CO_2H)_2$. *Carboxy-racemic acid.* Its ether is formed, together with a syrupy isomeride (Brunner, *B.* 12, 542) and other products, by the action of 3 p.c. sodium-amalgam on cold oxalic ether. After saponification by KOH the free acid is obtained by exactly neutralising the Ba salt by H_2SO_4 and evaporating at 45° (Löwig, *J. pr.* 79, 455 ; 83, 139 ; 84, 1; Klein, *J. pr.* [2] 20, 146).

Properties.—Hygroscopic crystalline mass (containing aq). V. e. sol. water and alcohol. Decomposed by heat. Its solution evolves CO_2 on evaporating above 50°, leaving racemic acid.

Salts.—Na_3A'''.—K_2HA'''. S. 5·2 at 16°: crystalline crusts.—K_3A''': gummy.—$Ba_3A'''_2$ 2aq. —$Ca_3A'''_2$ 3aq.—$Pb_7A'''_2O_4$.—Ag_3A'''.

Ethyl ether Et_3A''': [85°]. S. 10 at 16°. Triclinic crystals, $a{:}b{:}c = \cdot422{:}1{:}\cdot757$; $\alpha = 84°\,27'$, $\beta = 90°\,32'$, $\gamma = 90°\,6'$.

Acetyl derivatives $C_5H_5AcO_8$ and $C_5H_4Ac_2O_8$ are non-hygroscopic oils, not decomposed at 120°.

Benzoyl derivatives $C_5H_5BzO_8$ and $C_5H_4Bz_2O_8$ are oils, not decomposed at 140°.

Amide. Amorphous (Brunner).

DESOXY-AMALIC ACID *v.* Amalic acid.

DESOXY-BENZOIN *v.* Phenyl benzyl ketone.

DESOXY-CHOLIC ACID *v.* Cholic acid.

DESOXY-CODEÏNE *v.* Codeïne.

DESOXY-CUMINOÏN *v.* Cuminoïn.

DEUTERO-ALBUMOSE *v.* Proteids.

DEXTRANE $C_6H_{10}O_5$ (at 130°). $[\alpha]_D = 223°$. A gummy substance occurring in unripe beetroot (Scheibler, *J. T. C.* 1875, 790). Formed also in the lactic fermentation of sugar (Tieghem, *Jahres. d. Agriculturchemie*, 1879, 544). Amorphous; v. sol. water, forming a sticky liquid. Insipid taste. Its conc. aqueous solution is ppd. by lead subacetate, and gives with Fehling's solution a light-blue sticky pp., no reduction taking place. Boiling dilute H_2SO_4 converts it into glucose. HNO_3 gives oxalic acid only. Iodine gives no colouration.

Animal dextrane $C_6H_{10}O_5$. $[\alpha]_D = 157°$. Secreted by *Schizoneura lanuginosa*, a louse that forms galls on elm trees. Amorphous. Sl. sol. cold, more sol. boiling, water, insol. alcohol and ether. Fehling's solution gives a gelatinous coagulum, without reduction. Iodine gives no colour. Boiling dilute H_2SO_4 gives a substance that reduces Fehling's solution (L. Liebermann, *Pf.* 40, 454).

DEXTRIN $nC_{12}H_{20}O_{10}$. Although this term has been in use for a long time, and a correct percentage composition stated for the body it represents, it is only recently that its characters have been more accurately defined, and a place given to it among chemical compounds. Most of the substances to which the term has hitherto been given have many properties in common with dextrin, but it is evident that many of these hold no relation to it, and many more of them are impure conditions of it.

Occurrence.—(*a*) Dextrin is said to be present in the sap of plants and in most seeds. The evidence of this is, however, altogether unsatisfactory, other bodies possessing some of its properties being in most cases mistaken for it.—(*b*) It is a constituent of the juice of horse-flesh (Limpricht, *J.* 1865, 673), and it is probable, though not proved, that the body therein found is true dextrin.—(*c*) Reichardt (*Ar. Ph.* [3] 5, 502) states that the urine of diabetic patients, under certain conditions, contains dextrin; but from his description it is impossible to say whether the body he had under observation was dextrin or not.—(*d*) Dried starch, heated to 210° and maintained at that temperature for some time, yields a product known as British gum or commercial dextrin.—(*e*) By moistening the starch with dilute nitric acid, and drying before heating, this conversion is expedited.—(*f*) Digestion with dilute acids, inorganic and organic, converts starch into dextrin and other bodies. The commercial products from these sources contain dextrin or dextrins, but there are no analyses of them to show what dextrins they contain. For the action of heat and acids on starch see Biot and Persoz, *A. Ch.* [2] 52, 72; Payen, *ibid.* 55, 225; 61, 372; 65, 225, 334; Guérin-Varray, *ibid.* 60, 68; Jacquelain, *ibid.* [3] 8, 225; Béchamp, *C. R.* 51, 256; Anthon, *D. P. J.* 218, 182; 219, 457; O'Sullivan, *C. J.* 25, 581.—(*g*) When starch paste is submitted to the action of the unorganised ferment found in germinated grain, and known as diastase, dextrins, among other substances, are produced. It is one of the bodies derived from this source upon which we shall look as a chemical entity, and describe as dextrin; and it is only in as far as the bodies hitherto called dextrin, and obtained from the various sources above mentioned, agree in properties with those we shall find this to possess that we can consider them dextrin.—(*h*) Dextrin is found in beer, and is probably present in bread, being the product of the action of diastase on starch.—(*i*) Cellulose is converted into dextrin by the action of sulphuric acid (Branomot, *A. Ch.* 12, 172), but the identity of the body thus produced is not established.—(*j*) Dextrose is said to be converted into dextrin (Musculus, *Bl.* [2] 18, 66) by submitting the sulpho-glucosic acid to the action of spirit containing 95 p.c. alcohol. This, from its optical activity, is not pure dextrin.

Preparation.—100 grams of carefully purified potato starch (any other starch would answer, but this is most easily manipulated) are stirred up with 200 c.c. of water at 55°-60°, and as soon as the granules are thoroughly dispersed through the liquid 400 to 500 c.c. of boiling water are added with continual stirring. In this way an almost transparent and perfectly homogeneous paste is obtained. This is cooled to 62°, and a solution containing, in 50 c.c., 1 to 1·5 grams diastase,[1] or its equivalent in cold malt-extract added to it, and the mixture maintained at 60°-63° until the filtrate from a portion cooled no longer gives a colouration with iodine, and it is found that the optical activity of the solid matter in solution (*v.* SACCHARIMETRY) is $[\alpha]_j = 176{\cdot}6°$ (O'Sullivan, *J. C.* [2] 17, 125), 166·7° (Brown a. Morris, *ibid.* 47, 527). If the diastase is fairly active, and the proportion above given employed, this point is reached in five minutes' digestion or less; but inasmuch as, if the diastase is not very active, no further conversion to any extent takes place in a moderate time, the digestion may be continued for 15 or 30 minutes without any injurious effect. The solution is then cooled and filtered, to remove a slight turbidity due to a little flocculent matter from the diastase and impurity from the starch or undissolved, because ungelatinised, starch. The filtrate is then quickly boiled and evaporated, best under diminished pressure in a vacuum vessel, to about 200 c.c., and alcohol (S.G. ·83) added until a precipitate begins to form; a little more alcohol is added, and the mixture allowed to stand until the syrupy layer collects at the bottom. The clear supernatant liquid is decanted off, and the syrup washed with alcohol. This is dextrin more or less contaminated with maltose and a constituent of the diastase; the former can be completely, but with difficulty, separated by repeatedly dissolving in water, and carefully precipitating with alcohol in the least possible excess, until a portion of the precipitate, dissolved in water, no longer gives a reaction when boiled for three or four minutes with Fehling's solution. The diastase bodies are separated also with difficulty: the precipitate, freed from maltose, is dissolved in a little water and alcohol gradually added, until 5 to 10 p.c. of the whole is precipitated, pure dextrin remains in the supernatant liquid, and is precipitated from it by strong alcohol. To obtain it in the dry state the precipitate is treated with absolute alcohol, which extracts water from it, and renders it capable of being rubbed down to a white hygroscopic powder. The dextrin thus dried retains alcohol with much pertinacity, and if it be required to obtain a preparation absolutely free from that body, the powder must be dissolved in a little water, and boiled in a vacuum vessel until all alcohol is eliminated, and the solution reduced to a thick syrup. It is then transferred, in small quantities at a time, to an evaporating dish, and, while hot, placed under the bell glass of an air-pump over sulphuric acid and the air pumped out. If the syrup was sufficiently thick it swells up and blows out from loss of water. When this cools it becomes a porous, brittle, glassy mass, which can be rubbed down to a white powder if allowed to stand over sulphuric acid for a day or two, or in a few hours if the temperature of the dish be maintained by a steam coil in the air-pump receiver. Brown and Morris, acting on a suggestion of Wiley (*C. N.* 46, 175), propose to remove the last traces of maltose by treating a solution of the impure dextrin with a slight excess of a solution containing equal weights of mercuric cyanide and caustic soda until no further reduction takes place. This product would have to be purified from the materials employed, from the decomposition products, &c. This could probably be accomplished by neutralising with hydrochloric acid, evaporating to a syrup in a vacuum vessel, and submitting to dialysis, precipitating the dextrin in the concentrated solution with alcohol, and further purifying by partial precipitation with some reagent until the optical activity of the chief product becomes constant.

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[1] It is impossible to state an exact quantity of the preparation of diastase or of cold malt-extract, because the activity of the extract from a definite quantity of malt, and of the preparation of diastase, varies very considerably. A few experiments will, however, be sufficient to determine the quantity of either necessary to transform starch paste into products having an optical activity $[\alpha]_j = 177°$.

Properties.—Dextrin is uncrystallisable; dried as described above, it is a glassy, colourless body, capable of being rubbed down to a white powder. It is without marked taste, and is colourless. Its solutions are neutral. It is easily soluble in water, and solutions containing as much as 80 p.c. of the body, although syrupy, are thin-fluid. It is slightly soluble in dilute spirit, but insoluble in spirit containing 60 p.c. alcohol. It is not coloured by iodine. Exposed to moist air, and then allowed to stand over sulphuric acid, its weight becomes constant, when it contains from 9·5 to 10 p.c. water. This is almost completely lost in a vacuum over sulphuric acid, and completely in a current of dry air at 100°. The quantity of water corresponds to the formula $n(C_{12}H_{20}O_{10}2OH_2)$, and the amount of carbon and hydrogen yielded by the dry body agree well with the formula $C_{12}H_{20}O_{10}$. It is not precipitated by lime or baryta water, but it forms compounds with those earths which are insoluble in alcohol. It is precipitated by ammoniacal lead acetate, but not by the neutral or basic salt alone. Dilute sulphuric acid converts dextrin into maltose, and thence into dextrose, according to the equations $C_{12}H_{20}O_{10} + OH_2 = C_{12}H_{22}O_{11}$ and $C_{12}H_{22}O_{11} + OH_2 = 2C_6H_{12}O_6$. The phases of this reaction have as yet not been fully worked out. Diastase converts it slowly into maltose. Nitric acid converts dextrin into saccharic and oxalic acids. With a mixture of nitric and sulphuric acids it yields a nitrate, $C_6H_8(NO_2)_2O_5$, dinitrate according to Béchamp. By dissolving dextrin in acetic anhydride, and heating to 160°, triacetyl dextrin is produced (Schutzenberger a. Naudin, *C. R.* 68, 814), but these substitution products require further investigation. A solution of 10 grams dry dextrin in 100 c.c.—a vessel holding exactly 100 grams water at 15·5 —has a S.G. 1·0396, and its apparent optical activity is $[\alpha]_j = 222$, $= [\alpha]_D = 200{\cdot}4$. These are good working factors; but a careful and accurate determination of them is yet required. Under the influence of ordinary saccharomyces it is not converted into alcohol (fermented) in a moderate time; in presence of active diastase and this organism it ferments easily. Besides the dextrin here described, there are other dextrins to be found amongst the products of the action of diastase and of acids upon starch (*v.* STARCH), but experimenters with these bodies are not yet agreed as to their number or properties. Most of the properties just described are common to all the dextrins; but the distinguishing character of the dextrin of which we write is the action of diastase upon it. When a solution containing dextrin and diastase, in the proportion of 1 of the latter to 100 of the former, is digested at 60°-63° no more maltose is formed in the first five minutes than in the second five, in proportion to the amount of dextrin in solution, the conversion being a very slow and gradual process.

It may be fairly said that the opinions of Bondoneau (*C. R.* 81, 972, 1210) and those of Musculus and Gruber (*Bl.* 30, 54) have been shown to be untenable. The former describes *three* dextrins with different optical activities and powers of reducing copper oxide; the latter mentions *three* not coloured by iodine, of different optical activity, two having the same reducing power, and the third a higher power. O'Sullivan (*C. J.* 35, 770) isolated and described *three*, and indicated the existence of a fourth dextrin, all possessing the same optical activity as that given above, and being without reducing action on alkaline copper solution. Brown and Heron (*C. J.* 35, 596) and Brown and Morris (*ib.* 47, 527) maintain the evidence of eight dextrins without isolating any of them, but confirm O'Sullivan's observations that all the dextrins have the same optical activity $\alpha_j = 222$, and that they are without action on alkaline copper solution. The β-dextrin-iii of O'Sullivan, and the final dextrin of Brown and Morris, agree in properties; it is the dextrin described. All the dextrins are white, glassy, friable bodies, v. sol. water, and insol. strong alcohol. O'Sullivan characterises the dextrins as follows:—*α-dextrin*, coloured by iodine reddish-brown, unacted upon, or but slightly, by diastase at 69° 70°; at 66°–67°, 17·4 p.c., on transformed products, of maltose is produced in four to ten minutes, there being no increase in the next two hours if the diastase is not in excess and the temperature maintained; at 65°–66°, 34·5 p.c. maltose is formed; at 63°–64°, 51·2 p.c.; and below 62°, 67·8 p.c. This would indicate the molecule of this dextrin to be at least $C_{72}H_{120}O_{60}$. *β-dextrin*, not coloured by iodine. β-dextrin-i is not acted upon, or but slightly, by diastase at 66°; at 63°–64° it yields in five or ten minutes 34·6 p.c. maltose; at 61°–62° the same quantity is observed, and at 58°–59° there is no increase in the yield; this would indicate the formula $C_{36}H_{60}O_{30}$ for β-dextrin-i, if the formula of β-dextrin-iii be taken as $C_{24}H_{40}O_{20}$. According to Brown and Morris (*l.c.*) there are eight dextrins, beginning with $C_{108}H_{180}O_{90}$, each differing from the one below it by the group $C_{12}H_{20}O_{10}$, but they do not appear to have prepared any one of the bodies in a pure state. They determine the position in the series of an unknown one of them by the amount of maltose that it is capable of yielding when acted upon by diastase at 60° (*C. J.* 47, 543). All the high dextrins are acted upon in a fermenting solution, and yield maltose, and thence alcohol, the lowest dextrin being left. Although the researches referred to herein have thrown much light on the nature and character of the dextrin bodies, much still remains to be done before we can consider our knowledge complete.

Estimation.—In substances from which dextrin has not hitherto been isolated, and in which its presence is suspected from the optical activity of their solution, or the nature of their source, before any attempt at estimation is made, it would be necessary to prove its presence by eliminating the bodies with which it may be accompanied by processes indicated above, and comparing the properties of the body isolated with those herein given for dextrin. The estimation may then be effected after the manner indicated below, attention being given to the nature of the bodies with which it may be accompanied. In products in which the presence of dextrin is well established, viz. the various commercial sugars obtained by the action of acids on starch, malt-extract, beer, and such products, dextrin is estimated as follows:—*In the commercial starch sugars* a known weight of the sugar (15 g. or thereabouts is a suitable quantity) is dissolved in a small quantity of boiling water, the solution cooled and then made up to 100 c.c. This is submitted to fermentation with 0·5 g. yeast, and the fermentation pushed as far as possible. The alcohol is eliminated by distillation, the residue filtered and made up to 100 cc. with the washings; of this an optical activity is taken and K determined (*v.* SACCHARIMETRY); if the latter indicates more than 15 p.c. calculated on the solid matter unfermented, the solution must again be submitted to fermentation, and the amount of reducing sugar further diminished; if less, the reducing body may be taken as maltose, and the calculation made accordingly.

Example.—15 g. glucose syrup dissolved to 100 c.c., submitted to fermentation with 0·5 g. yeast, yielded 100 c.c. of residue of S.G. 1·0012 = about 3·038 g. solid matter per 100 c.c. 18·57 g. of this solution yielded 0·087 g. CuO; this corresponds to ·087 × ·7256 [1] = ·0631 g. maltose, and to a total amount of maltose in the 100 c.c. of $\frac{100·12 \times ·0631}{18·57} = ·3402$ g., or to ·087 × ·4535 = ·0394 g. dextrose, giving a total amount of dextrose in the 100 c.c. of $\frac{100·12 \times ·0394}{18·57} = ·2124$ g. This is less than 15 p.c. on the solid matter in solution, hence the reduction found above is taken as maltose. The optical activity of the solution was 26·5 divisions of a Soleil-Ventzke-Scheibler saccharimeter; this corresponds to $\frac{26·5 - ·34 \times 8·02}{11·56} = 2·143$ dextrin, and as the solid matter was found to be 82·0 p.c. of the syrup the dextrin is 17·4 p.c. of the solid matter. In beer the estimation is made in the same way, only, as a rule, in a beer of any age the cupric oxide reduced may be calculated as maltose without further consideration, a correction of ·0008 g. being subtracted from the weight of CuO for every gram of beer taken for the reduction. In malt-extract the estimation is effected in the same manner as described for sugar syrup above, the procedure after fermentation being the same as followed in the case of beer. Should active diastase be present in the malt-extract, as is usually the case in the best preparations, the solution should be boiled before fermentation. According to Wiley (*C. N.* 46, 175) dextrin can be estimated in the starch products by eliminating the reducing bodies by alkaline solution of mercury dicyanide. He proceeds as follows:—The mercury solution is made by dissolving 120 g. $HgCy_2$ and 120 g. NaOH in water, and making up to 1 litre. 1 g. of the sugar to be examined is dissolved in 10 c.c.; this is boiled for two or three minutes with an excess of the mercury solution, of which 25 c.c. will as a rule be found sufficient. The solution is cooled, neutralised with HCl, and the bulk made up to 50 c.c. An observation of the optical activity of this solution gives the dextrin. For example, the optical activity of a solution, prepared as described, and observed in a 200 mm. tube, was found to be 2·3 divisions of a S.V.S.

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[1] CuO × 0·7256 = maltose corresponding to CuO.

saccharimeter—2·3 ÷ 11·56 = 20 g. dextrin in 100 c.c., *i.e.* ·1 g. in 50 c.c. 1 g. sugar yields ·1 g. dextrin or 10 p.c. (Further on this subject *v.* SACCHARIMETRY.) If any of the higher dextrins should be present the quantity could be approximately estimated by the action of malt-extract at the various temperatures indicated above, and the position and approximate quantity of the dextrin inferred from the amount of maltose formed in five to ten minutes. C. O'S.

DEXTRO-. Compounds beginning with this prefix, indicating a right-handed rotatory effect on light, are described under the remaining part of the name; *e.g.* dextro-tartaric acid under TARTARIC ACID.

DEXTRONIC ACID *v.* GLUCONIC ACID.

DEXTROSE *v.* SUGARS.

DI-. When this prefix is used in a numerical sense it is entirely left out of account in determining the alphabetical position assigned to a compound in this dictionary.

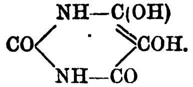
DIALURIC ACID $C_4H_4N_2O_4$ *i.e.* $CO<\begin{smallmatrix}NH.CO\\NH.CO\end{smallmatrix}>CH.OH$. *Tartronyl-urea.* Mol. w. 144.

Formation.—1. By passing H_2S through a boiling aqueous solution of alloxan (Liebig a. Wöhler, *A.* 26, 276).—2. By treating alloxan with zinc and HCl.—3. By dissolving uric acid in dilute HNO_3 and adding ammonium sulphide. 4. By treating an aqueous solution of alloxan with ammonium or potassium cyanide (Strecker, *A.* 113, 49).—5. By treating alloxantin with sodium amalgam (Baeyer, *A.* 127, 12).—6. By treating di-bromo-barbituric acid with H_2S (Baeyer, *A.* 130, 133).

Properties.—Needles, sl. sol. water, acid to litmus. Oxidised by moist air to alloxantin. Combines with alloxan forming alloxantin. Heated with glycerin at 100° it forms hydurilic acid.

Salts.—NH_4A': silky needles; converted at 100° into blood-red murexide.—KA' (*cf.* Menschutkin, *A.* 182, 70). Urea dialurate $CON_2H_4C_4H_4N_2O_4$: stellate crystals (Mulder, *B.* 6, 1010).

Iso-dialuric acid



$$CO<\begin{matrix}NH-C(OH)\\ \\NH-CO\end{matrix}>COH.$$

Iso-tartronyl urea. Formed by the action of bromine water on isobarbituric acid, amido-uracil, or hydroxanthine (Behrend a. Roosen, *B.* 21, 1000). Prisms (containing 2aq). V. sol. water. Stable towards oxidising agents. Is converted by warming with urea and conc. H_2SO_4 into what is believed to be uric acid.

DIALYSIS. The separation of certain substances by liquid diffusion; *v.* DIFFUSION and PHYSICAL METHODS, vol. iv. p. 172.

DIAMOND *v.* CARBON, vol. i. pp. 685, 686, 687.

DIASTASE C 44·33, H 6·98, N 8·92, S 1·07, O 32·91, ash 4·79. The substance that enables malt to convert starch into dextrin and sugar. Green barley malt is digested with dilute alcohol (20 p.c.) for 24 hours; the extract is ppd. with 2½ vols. absolute alcohol, and the pp. washed with alcohol and ether (O'Sullivan, *C. J.* 45, 2; Lintner, *J. pr.* [2] 34, 386; 36, 481).

Purification.—Cannot be purified by ppg. with basic lead acetate (L.); purified by repeated solution in water and ppn. with alcohol; the ash can be reduced by dialysis to less than 5 p.c. consisting of calcium phosphate.

Properties.—Amorphous; has not been obtained pure. Its action on starch is prevented by strong acids or alkalis, by salts of Cu, Hg, and Ag, by alum, and by Fe_2Cl_6, but not by phenol. Hydroxylamine, formic aldehyde, and nitrous acid at 40° render diastase inactive (Loew, *J. pr.* [2] 37, 101). Presence of CO_2 accelerates the power of diastase to convert starch into sugar (Baswitz, *B.* 11, 1443). Above 63° the fermenting power is weakened.

Reactions.—1. Does not reduce Fehling's solution even after boiling with HCl.—2. Does not give a violet colour with $CuSO_4$ and KOH.—3. Ppd. by boiling.—4. HCl gives a pp., sol. NaOH.—5. HOAc a pp. sol. excess.—6. $HgCl_2$ a pp.—7. Basic lead acetate a pp.—8. HOAc and K_4FeCy_6 a pp.—9. Millon's reagent gives albumen reaction.—10. Warmed with fuming HCl a violet colour.—11. Guaiacum tincture mixed with a little H_2O_2 gives a blue colour.

References.—Payen a. Persoz, *A. Ch.* [2] 53, 73; 56, 237; 60, 441; 61, 351; Guérin-Varry, *A. Ch.* 57, 108; 60, 22; 61, 22; Bouchardat, *A. Ch.* [3] 14, 61; Fankhauser, *Bied. Centr.* 1888, 205; Defresne, *C. R.* 89, 1070; Brasse, *C. R.* 100, 454; H. Muller, *Ann. Agronom.* 12, 481; Bourquelot, *C. R.* 104, 576; Kjeldahl, *C. J.* 38, 562; Zulkowski a. Renner, *C. J.* 38, 561; *B. C.* 1879, 929; Schärtler, *C. C.* 1887, 534; Huppe, *C. J.* 44, 101; Schneider, *C. J.* 46, 1366; Herzfield, *B. C.* 10, 203; Stutzer a. Isbert, *H.* 12, 72).

V. also FERMENTATION, DEXTRIN, STARCH, and SUGARS.

Diastase *of Kôji.* Kôji is used in Japan to make beer. It is formed by steaming rice-grains and leaving them till a fungus grows on them. An aqueous infusion of this Kôji acts somewhat like malt-extract, for it inverts cane-sugar and hydrates maltose and dextrin, and it liquefies starch paste, forming first maltose and dextrin, then glucose and dextrin (R. W. Atkinson, *Pr.* 31, 523; 32, 299). The diastase-like ferment is obtained from the albuminous matters in the rice through changes produced by the growth of the fungus.

DIATEREBIC ACID *v.* TEREBIC ACID.

DIATEREBILENIC ACID *v.* TEREBILENIC ACID.

DIATERPENYLIC ACID *v.* TERPENYLIC ACID.

DICHROÏNS. A name given by Brunner and Chuit (*B.* 21, 249) to the fluorescent colouring matters obtained in Liebermann's reaction by treatment of phenols with conc. H_2SO_4 and nitrous acid. They are obtained by the action of H_2SO_4 saturated with nitrous acid on para-nitrosophenols; but only those polyhydric phenols having the hydroxyl-groups in the meta-positions to one another yield dichroïns. The dichroïns are divided into (α)-dichroïns containing the complex $C_6.N:(O.C_6)_2$, and (β)-dichroïns with the group $C_6.N<\begin{smallmatrix}O\\O\end{smallmatrix}>C_6$. The colouring matters $C_{18}H_{15}NO$ from phenol, $C_{18}H_{13}NO_6$ and $C_{36}H_{26}N_2O_{10}$ from resorcin, and $C_{21}H_{21}NO_6$ from orcin belong to the (α)-group, whilst the (β)-group includes $C_{14}H_{11}NO_3$ from orcin, azoresorcin, azoresorufin, and azoresorufin ether; the last three are respectively (β)-resorcin-, di-(β)-resorcin-, and tetra-(β)-resorcin-dichroïn (H. Brunner and P. Chuit, *B.* 21, 2479).

Chroïns.—Chroïns are colouring matters resulting from the action of H_2SO_4 containing nitrous acid on nitroso-phenols, which are analogous to the quinoneoximes, and they appear to contain the $(C_6)_2$:N—O—N:$(C_6)_2$.

Oxychroïns.—Oxychroïns are bodies bearing a similar relation to nitro-phenols as dichroïns do to nitroso-phenols. They are obtained in most reactions along with the dichroïns during the preparation of the latter. They are richer in oxygen than dichroïns and do not fluoresce.

DICHROÏSM. The property exhibited by many doubly refracting crystals of showing different colours when examined in different directions.

DICHROMATES. Salts of the hypothetical acid $H_2Cr_2O_7$ *v.* CHROMIUM, ACIDS OF, p. 154, 157.

DICONIC ACID $C_9H_{10}O_6$. [200°]. Formed by heating citric acid with conc. HClAq at 200° (Hergt, *J. pr.* [2] 8, 372); aconitic acid seems to be an intermediate body. Small crystals, v. sol. water, alcohol, and ether. Reddens litmus.

Salts.— K_2A'': deliquescent. — $(NH_4)_2A''$: [95°]; deliquescent crystalline mass.—$BaA''1\frac{1}{2}aq$: more sol. cold than hot water.—$BaH_2A''_2$.—SrA'' 5aq.—CaA'' aq.—MgA'' 6aq: hard crystalline crusts, v. sol. water.—$Fe(OH)_2HA''$ (?).—MnA'' 5aq: plates. — CoA'' 6aq: rose-coloured monoclinic plates.—NiA'' 6aq.—ZnA'' 6aq: monoclinic plates. — $ZnH_2A''_2$7aq. — CuA'' 3aq: bluish-green prisms.—$SnA''SnO$ 4aq: insoluble pp.

Diethyl ether Et_2A''. Oil.

DIDYMIUM Di. At. w. 143 (exact value doubtful). Mol. w. unknown. S.G. 6·544. S.H. ·04563 (Hillebrand, *P.* 158, 71). Melts above Ce and La. In 1842 Mosander separated a new metal from the mineral *Cerite* (*P.* 56, 503); as the metals Ce and La had already been found in this mineral, the name *didymium* was given to the new metal to suggest its close relationship to lanthanum (δίδυμος = two-fold). Recent investigation has succeeded in obtaining from certain Di salts what seem to be two classes of compounds distinguished by their absorption-spectra and colour; these compounds in all probability are salts of two distinct elements (*v. infra*); the name *didymium* is therefore a singularly happy one. In the present state of knowledge of the rarer elements it seems well to describe the body regarded until recently as a single element, and the compounds of this body.

Occurrence.—As silicate in various Scandinavian and Siberian minerals, *Cerite*, *Gadolinite*, *Orthite*, &c., accompanying Ce and La.

Preparation.—The mixed oxides of Ce, La, and Di are separated from *Cerite* by treatment with H_2SO_4, &c., as described under CERIUM (vol. i. p. 723); Ce is then separated as basic nitrate by one of the methods described under CERIUM. The solution of Di and La nitrates may then be treated in different ways: Bunsen a. Jegel (*P.* 155, 377) recommend ppn. of the hydrated oxides of Di and La by NH_3Aq, solution in H_2SO_4Aq, evaporation, and crystallisation of the sulphates; the sulphates are then dried and powdered, 1 part is dissolved in small successive portions in 6 parts water at 2°-3°, the solution is heated to c. 40°, when La_23SO_4 separates, the mother-liquor is slowly evaporated by standing in a warm place, when rose-coloured rhombohedra of Di_23SO_4 separate; thin violet plates generally also form on the sides of the dish, these are a mixture of the two sulphates, they are easily distinguishable from the Di_23SO_4 crystals; the rose-coloured crystals are picked out, and purified by re-crystallisation (Mosander, *P.* 56, 503, or *P. M.* 28, 241). The crystals thus obtained usually contain a little La_23SO_4; Hermann (*J. pr.* 82, 385) evaporates the solution of Di_23SO_4 containing some La_23SO_4 to dryness at about 18°-20°, adds a little cold water to the residue which dissolves Di_23SO_4 with very little La_23SO_4, evaporates to dryness at 18°-20°, treats with cold water, &c., and repeats these operations so long as there is any residue not quickly sol. in a little cold water. To complete the separation, Hermann (*l.c.*) dissolves the Di_23SO_4, which may contain traces of La_23SO_4, in water, divides the solution into two parts, ppts. one part by NH_3Aq, washes the pp. thoroughly, mixes it while moist with the other part of the solution, and allows the whole to remain at a moderate temperature for some days; basic La sulphate thus dissolves completely and basic Di sulphate separates; after a few days the crystals which separate are collected, washed, dissolved in H_2SO_4Aq, and again crystallised (*v.* also Erk, *Z.* [2] 7, 104).

Other methods for separating Di salts from La salts are based on the relative solubilities of the oxalates and nitrates of the two metals; *v.* Marignac, *A. Ch.* [3] 27, 226; Holzmann, *Zeitschr. für Chem. und Pharm.* 1862. 668; Zschiesche, *J. pr.* 107, 65; Frerichs a. Smith, *A.* 191, 331. Frerichs (*B.* 7, 798) describes a method of separation founded on the reaction between $DiCl_3$ and LaOCl, whereby Di_2O_3 and $LaCl_3$ are produced.

According to Cleve (*C. J.* 43, 362) the Di_23SO_4 prepared as described may still contain samarium salts; samarium oxide is separated by long continued fractional ppn. with cold dilute NH_3Aq, the earlier fractions are rich in samaria, the later are chiefly didymia; by solution of the later portions in HNO_3Aq and repeated fractional ppn. by dilute NH_3Aq, didymia is at last obtained free from samaria. (Cleve's paper contains a description of a method for the approximate separation of the rare earths, which he says is very convenient.)

The Di_23SO_4 purified as described is dissolved in water, and NH_3Aq is added in excess, the ppd. hydrate is washed, and dissolved in HClAq, the liquid is evaporated after addition of NH_4Cl, and the residue is heated; nearly pure $DiCl_3$ containing a little DiOCl is obtained. The $DiCl_3$ may be reduced by heating with K in a porcelain tube; on washing with water small particles of Di are obtained (Marignac, *A. Ch.* [3] 38, 148); the reduction is better effected by mixing with NaCl, melting, and electrolysing (Hillebrand a. Norton, *P.* 155, 633).

Properties and Reactions. — White metal, malleable and ductile, harder than Ce. Oxidises in air; when finely divided it burns in a flame with production of much light; dissolves readily in dilute HClAq, HNO_3Aq, and H_2SO_4Aq; decomposes cold water slowly and hot water rapidly.

The atomic weight of Di has been determined (1) by analysing the sulphate (Marignac, *A. Ch.* [3] 27, 231; Erk, *Z.* [2] 7, 106); (2) by analysing the chloride (Marignac, *A. Ch.* [3] 38, 153); (3) by transforming the oxide into sulphate, or *vice versâ* (Hermann, *J. pr.* 82, 387; Erk, *Z.* [2] 7, 106; Zschiesche, *J. pr.* 107, 65; Cleve, *Bl.* [2] 21, 246; 39, 289; *C. J.* 43, 362; Brauner, *C. J.* 41, 68, and (later) *W. A. B.* 3, 141, 499); (4) by determining S.H. of Di, Hillebrand a. Norton (*P.* 158, 71). The numbers obtained for the atomic weight of Di vary from c. 145 to c. 142; Cleve thinks that the value 142·124 ± ·0326 may be accepted; Brauner thinks that Di = 145·2 to 145·4 (*C. J.* 43, 288).

Separation of didymium into different constituents.—La-NH_4 nitrate is more sol. HNO_3Aq than Di-NH_4 nitrate; when a long process of fractional crystallisation is conducted with a mixture of these salts, the La salt may be completely removed, and at the same time the Di salt separated, according to v. Welsbach, into two perfectly distinct compounds (*Sitz. W.* 92 [2nd part], 317). A large quantity of the mixed nitrates of La and Di obtained from *cerite* after separating basic Ce nitrate (*v.* vol. i. p. 723) is mixed with the necessary quantity of NH_4NO_3, about $\frac{1}{10}$th part conc. HNO_3Aq is added, and the liquid is evaporated until small crystals appear on the surface, a little water is added, and crystallisation is allowed to proceed for about 24 hours; the crystals are drained and washed with a little HNO_3Aq which is added to the mother-liquor; the mother-liquor is evaporated and crystallised; the liquor from this is again evaporated, and so on until 6–8 fractions have been obtained; these fractions are then systematically refractionated by crystallisation from HNO_3Aq several thousand times. Two nitrates are finally obtained, one forming a pale-green solution, the other forming a rose-coloured solution; these solutions give different emission- and absorption-spectra, the sum of the two spectra is the same as the spectrum of didymium nitrate. From each solution salts are obtainable, one series is green, the other is rose-coloured; by decomposing the green nitrate by heat a brownish-black oxide is obtained, and by decomposing the rose-red nitrate a blue-grey oxide is produced; analyses of the oxides and salts are not given in the original paper. For the element which forms green salts v. Welsbach proposes the name *praseodymium*, and for that which gives rose-coloured salts he proposes the name *neodymium*; he assigns the atomic weight 143·6 to praseodymium, and the atomic weight 140·8 to neodymium, the oxides having the composition M_2O_3. When a salt of praseodymium is mixed in certain proportions with a salt of neodymium, the spectrum of the mixture is the same as that of didymium.

Becquerel (*C. R.* 104, 1691; 777) has examined the absorption-spectra of Di salts, and concludes that these salts are mixtures of at least two substances. Brauner (*C. J.* 43, 281) got indications of the complex nature of Di by careful fractional ppn. of $Di3NO_3$ solution by NH_3Aq. Crookes (*N.* 34, 266) did not succeed in separating v. Welsbach's praseo- and neodymium from didymium; he thinks that these names may represent two different groups of molecules into which what is called didymium is separated by one particular method of fractionation.

Chemical relations of Didymium.—If the body called didymium is an elementary substance, it must be placed in Group V. with N, P,...and Bi. Di forms the oxide Di_2O_3, and probably Di_2O_5, but only one class of salts Di_23X where $X = SO_4, 2NO_3$, &c.; one class of haloid salts is known, DiX_3, where X = F, Cl, Br; the oxychloride DiOCl has been prepared. Di is more closely analogous to Bi than to any other element of Group V.

Didymium arsenate *v.* vol. i. p. 308.

Didymium bromide $DiBr_3.6H_2O$. Violet, deliquescent crystals; S.G. 2·81 (Cleve, *Bl.* [2] 39, 289); obtained by dissolving Di_2O_3 in HBrAq and evaporating over H_2SO_4. Forms double salts (Frerichs a. Smith, *A.* 191, 342): $2DiBr_3.3NiBr_2.18H_2O$; $2DiBr_3.3ZnBr_2.36H_2O$ ($24H_2O$ according to Cleve, *Bl.* [2] 39, 289), very deliquescent; $DiBr_3.AuBr_3.10H_2O$ (Cleve, *l.c.*).

Didymium chloride $DiCl_3.6H_2O$. Violet, deliquescent, monoclinic crystals; very soluble in water or alcohol; S.G. 2·286 (Cleve, *l.c.*). Obtained by dissolving Di_2O_3 in HClAq, evaporating, and crystallising; when the solution is evaporated to dryness after addition of NH_4Cl and the residue is heated, or when the residue obtained by evaporating Di_2O_3 in HClAq to dryness is heated in a stream of HCl, nearly pure $DiCl_3$, containing a little DiOCl, is obtained.

Double salts.—$2DiCl_3.3AuCl_3.2H_2O$: brilliant yellow deliquescent plates, by evaporating a solution of the mixed chlorides (Frerichs a. Smith, *A.* 191, 340); $2DiCl_3.9HgCl_2.24H_2O$; $2DiCl_3.3PtCl_4.24H_2O$ (F. a. S.); $DiCl_3.PtCl_4.10\frac{1}{2}H_2O$, deliquescent prisms; S.G. 2·689 (Cleve, *Bl.* [2] 39, 289); $DiCl_3.SnCl_4.10\frac{1}{2}H_2O$ (Cleve, *Bl.* [2] 31, 196).

Didymium fluoride $2DiF_3.H_2O$; reddish pp. by adding HFAq to solution of Di acetate (Cleve). According to Frerichs a. Smith (*A.* 191, 343) the pp. formed by adding HFAq to Di_23SO_4Aq is $2DiF_3.3HF$; this is denied by Cleve (*B.* 11, 910).

Double salts.—Obtained by treating Di_2O_3 with KF.HF (Brauner, *C. J.* 41, 68); $2DiF_3.3HF.H_2O$; $3DiF_3.3KF.H_2O$; $4DiF_3.3KF$.

Didymium hydroxides *v.* DIDYMIUM, OXIDES AND HYDRATED OXIDES OF.

Didymium iodide. Not isolated. Frerichs a. Smith (*A.* 191, 343) obtained the double salt $2DiI_3.3ZnI_2.24H_2O$ as deliquescent yellow plates.

Didymium, oxides and hydrated oxides of. Di forms the oxide Di_2O_3; another oxide Di_2O_5, and another intermediate between these, Di_2O_4 or Di_4O_9, probably exists. The hydrated oxide $Di_2O_3.3H_2O$ seems not to have been obtained in a state of purity; $Di_2O_5.3H_2O$ has probably been isolated. The oxides and hydrated oxides of Di are basic; the higher oxides react with acids as peroxides, forming salts of the series Di_23X ($X = NO_3, \frac{SO_4}{2}$, &c.).

DIDYMIUM OXIDE Di_2O_3. S.G. 7·18 (Cleve, *Bl.* [2] 39, 289); S.H. ·081 (Nilson a. Pettersson, *B.* 13, 1459). Obtained by ppg. $DiCl_3Aq$ by KOHAq. and strongly heating the hydrated oxide thus formed; also by strongly heating $Di(NO_3)_3$, $Di_2(C_2O_4)_3$, or $Di_2(CO_3)_3$; it is advantageous to complete the decomposition in a stream of H to deoxidise any higher oxide formed. Greyish-blue solid (Cleve, *Bl.* [2] 39, 289); white without any blue tinge according to Hermann (*J. pr.* 82, 385). Unchanged by heating in H; probably combines with O when heated in that gas (*v. infra*). Emits white light when very strongly heated, the lines in the spectrum of the light emitted are the same as the dark lines in the absorption-spectrum of dilute Di salt solutions. Dissolves in acids to form salts Di_23X where $X = NO_3, \frac{SO_4}{2}$, &c. Insoluble in water, but in hot water forms a hydrate probably $Di_2O_3.3H_2O$. In ordinary air forms Di_23CO_3; decomposes hot solutions of NH_4 salts, evolving NH_3.

Hydrated didymium oxide ?$Di_2O_3.3H_2O$ ($=Di(OH)_3$). The pp. obtained by adding KOHAq or NaOHAq to solutions of Di salts is gelatinous, pale rose-red, insoluble in excess of the pptnt.; it always contains a little carbonate. NH_3Aq ppts. basic salts from solutions of Di salts. Thomsen gives the heat of neutralisation of didymium hydrate $[Di^2O^3.xH^2O,3H^2SO^4Aq] = 77,160$ (*Th.* 1, 375).

Oxides of didymium other than Di_2O_3. According to Frerichs a. Smith (*A.* 191, 344), Di_2O_3 prepared by gently heating $Di(NO_3)_3$ absorbs O when heated in that gas, forming a chestnut-coloured powder approximating to the composition Di_4O_9. The same chemists also obtained Di_4O_9 by heating $Di_2(C_2O_4)_3$ in a stream of O. Hermann (*J. pr.* 82, 385), by heating Di_2O_3 in O, obtained a product with only c. ·8 p.c. more O than Di_2O_3; Cleve (*B.* 11, 910) states positively that Di_4O_9 cannot be obtained as described by Frerichs a. Smith. Brauner (*C. J.* 41, 68) says that the oxide obtained by carefully heating basic Di nitrate to dull redness in a stream of O has the composition Di_2O_5; he describes this oxide as an amorphous chocolate-brown powder, soluble in dilute HNO_3Aq or dilute H_2SO_4Aq without evolution of gas, but soluble in more conc. acids with evolution of O, insoluble in HFAq, decomposed when strongly heated with production of O; reduced in H at low red heat; S.G. at 15° = 5·368; reacts with acids to form salts Di_23X, and must therefore be classed as a basic peroxide. Brauner (*l.c.*) ppd. a solution of $Di3NO_3$, containing H_2O_2, by dilute KOHAq and dried *in vacuo*, he thus obtained a light red powder to which he assigns the formula $Di_2O_5.3H_2O$. It is still uncertain whether Brauner's peroxide can be obtained from a specimen of $Di3NO_3$ perfectly free from samarium.

Didymium, oxyhaloid compounds of. The only one of these compounds definitely known is the *oxychloride*, DiOCl; it is a greyish powder, S.G. 5·751 (Cleve, *Bl.* [2] 39, 151), obtained by heating $DiCl_3.6H_2O$ and treating the residue with water (Marignac, *A. Ch.* [3] 38, 148), or, according to Frerichs a. Smith (*A.* 191, 341), by heating Di_2O_3 in Cl at 200°.

Didymium oxysulphide. Marignac (*A. Ch.* [3] 38, 148) describes a greyish powder, insoluble in water, obtained by heating Di_2O_3 with S and NaOH; he gives it the formula Di_2O_2S.

Didymium, salts of. Di forms one class of salts, Di_23X, where $X = NO_3, \frac{SO_4}{2}, \frac{1}{3}PO_4$, &c.; many of them are soluble in water, forming rose-red liquids; several double salts, but very few basic salts, are known. The chief salts are *borate, bromate, carbonate, chlorate, iodate, molybdate, nitrate, oxalate, phosphates, selenate and selenite, sulphate and sulphite, tungstate, vanadate*; *v.* Carbonates, Nitrates, Sulphates, &c.

Didymium sulphide Di_2S_3. A brownish-green powder; obtained by heating Di_2O_3 in H charged with CS_2 vapour. Decomposed easily by acids with evolution of H_2S; decomposed by heat to Di_2O_3 and basic Di sulphates (Marignac, *A. Ch.* [3] 38, 148; Frerichs a. Smith, *A.* **191**, 345).

Didymium sulphocyanide *v.* Sulphocyanides under Cyanides, p. 350. M. M. P. M.

DIFFUSION. The mixing or mutual interpenetration, by reason of the movements of the minute particles of the fluids, of gases or liquids which do not chemically interact, is called *diffusion*, whether the fluids are in immediate contact or are separated by porous partitions. When a liquid passes through a membrane into another liquid the process is generally called *osmotic diffusion* or simply *osmose*; when the diffusion of a liquid is accompanied by a separation, partial or complete, into two or more chemically different bodies, the process is generally known as *dialysis*. Substances which when in solution pass freely through a porous membrane, or readily diffuse into another liquid in contact with them, are generally called *crystalloids*, while those substances, solutions of which do not diffuse, or diffuse very slowly, are usually called *colloids*. For an account of *diffusion* and the applications of this process to chemical questions *v.* Physical methods, vol. iv. p. 172.

M. M. P. M.

DIGITALIN C 58·2 p.c.; H 3·7 p.c. S (cold 90 p.c. alcohol) 8½; (boiling 90 p.c. alcohol) 17. Occurs in the leaves of the common foxglove (*Digitalis purpurea*). It may be extracted from the leaves by dilute (50 p.c.) alcohol; the solution treated with basic lead acetate, and the filtrate, freed from excess of lead by Na_2CO_3, ppd. by tannin. The digitalin tannate is then decomposed by lead oxide and the liberated digitalin crystallised from alcohol (Lefert, *J. Ph.* [5] 6, 424; *cf.* Nativelle, *J. Ph.* [4] 9, 255; 20, 81; *Ph.* [3] 2, 865; Le Royer, *Bibl. Univ.* 26, 102; Lancelot, *A.* 12, 251; Trommsdorff, *A.* 24, 240; *Ar. Ph.* 10, 113; Homolle, *J. Ph.* [3] 7, 57; O. Henry, *J. Ph.* [3] 7, 460; Homolle a. Quevenne, *Mémoires sur la Digitaline*, Paris, 1851; *Répert. Pharm.* [3] 9, 2; Walz, *Jahrb. pr. Pharm.* 14, 20; 21, 29; 24, 86; 26, 296; *Gerh.* 4, 286; *N. Jahrb. Pharm.* 8, 332; 9, 302; 10, 319; *J.* 1847, 645; 1851, 567; 1852, 679; 1853, 568; 1857, 520; 1858, 528; Delffs, *N. Jahrb. Pharm.* 9, 26; *J.* 1858, 528; Kossmann, *J. Ph.* [3] 38, 5; [4] 20, 427; *C. J.* 28, 650; Flückiger, *N. Jahrb. Pharm.* 39, 129; *C. C.* 1873, 371; Goerz, *J.* 1873, 815; Schmiedeberg, *Ph.* [3] 5, 741; Morin, *J. Ph.* [3] 7, 294).

Properties.—Slender needles grouped around a common axis (Nativelle) or small minute plates (Flückiger). Insol. water and dilute alkali, v. sl. sol. ether, v. sol. chloroform, chloroform-alcohol, and acetic acid. Hydrochloric acid dissolves it, forming a yellowish solution, slowly becoming emerald-green. Conc. H_2SO_4 and H_3PO_4 also give green colours. Digitalin has no smell but a bitter taste. It is poisonous, acting on the heart. Split up by boiling dilute acids into glucose, digitaliretin (C. 66 p.c.; H. 4·6 p.c.), and other bodies (Kossmann). Treatment with H_2SO_4 (1 pt.) and alcohol (1 pt.) containing a few drops of aqueous Fe_2Cl_6 gives a greenish-blue solution (Lafon, *Bl.* [2] 44, 18). Digitalin, being a glucoside, colours a hot mixture of bile and H_2SO_4 red (Pettenkofer's reaction; *cf.* Brunner, *B.* 6, 96).

Digitaleïn C 53·2; H 8·1 p.c. An amorphous substance occurring in the leaves of *Digitalis purpurea* and *D. lutea.* V. sol. water and cold alcohol, sl. sol. chloroform, insol. ether. Ppd. from its aqueous solution by tannin or lead subacetate. Split up by dilute acids into glucose and digitaliretin. Narcotic poison.

Digitin $(C_4H_9O_2)_x$? Occurs in foxglove leaves. Stellate groups of needles, insol. water, chloroform, and benzene, v. sol. ether and alkalis (Goerz, *J.* 1873, 814).

Digitonin C 53·4 p.c.; H 7·5 p.c. A white amorphous substance occurring in foxgloves. Resembles saponin and melanthin. V. sol. water, forming a solution that froths on shaking. Ppd. from its aqueous solution by alcohol, baryta-water, or lead subacetate. Gives a red colour when boiling with dilute acids (Greenish, *Ph.* [3] 10, 909; 1013).

Digitoxin C 63·6 p.c.; H 8·1 p.c. Occurs in the leaves of the foxglove. Needles or tables, insol. water and benzene, sl. sol. ether, v. sol. alcohol and chloroform. Boiling dilute acids convert it into amorphous soluble toxiresin. Both digitoxin and toxiresin are very poisonous. According to Kopp digitoxin is eight times as poisonous as digitalin.

DILITURIC ACID *v.* NITRO-BARBITURIC ACID.

DILL OIL. S.G. ·9. (c. 190°). The volatile oil of *Apium* (or *Anethum*) *graveolens*. It contains carvene and carvol (Wallach, *A.* 227, 292; *cf.* Nietzki, *Ar. Ph.* [3] 4, 317; Gladstone, *C. J.* 17, 1; 25, 1).

DIMORPHISM and **TRIMORPHISM.** These terms are used to denote the existence of the same chemical substance, elementary or compound, in different crystalline forms. The two kinds of crystals of a dimorphous body, or the three kinds of crystals of a trimorphous body, may belong to different systems, *e.g.* carbon crystallises in the regular system as diamond and in hexagonal forms as graphite; nickel sulphate crystallises in trimetric prisms, in dimetric octahedra, and in monoclinic prisms; or the different crystals of the same body may belong to the same system, and yet so differ in their corresponding angles that they cannot be reduced to the same form; mono-sodium phosphate, for instance, $NaH_2PO_4.xH_2O$, crystallises in two different trimetric forms. Di- and tri- morphism is usually accompanied by differences of S.G., colour, hardness, or other properties (*v.* CRYSTALLISATION and ISOMORPHISM). M. M. P. M.

DIOSMIN C 53 p.c.; H 6·1 p.c. [243°].

Occurrence.—In the leaves of *Barosma crenata* and *betulina* (Cape of Good Hope).

Preparation.—The leaves are first extracted with petroleum to remove the essential oils together with chlorophyll, a wax and a resin; then they are extracted with cold, and finally with hot, alcohol (80–85 p.c.). The diosmin is obtained by heating with ammonium carbonate, and finally washing with alcohol and ether (P. Spica, *G.* 18, 1).

Properties.—White or yellowish-white crystals, insol. most solvents, but sol. hot alcohol (80–85 p.c.). In composition it is practically identical with hesperidin (Paternò a. Briosi, *G.* 6, 169). Reduces Fehling's solution. Dissolves in concentrated acids and alkalis, but is reppd. on neutralisation. Heated with concentrated mineral acid it is decomposed into a glucose and an orange-yellow crystalline substance [145°]. Shimoyama (*Archiv der Pharm.* 1887) considers the similar glucoside hesperidin to be present in the leaves of various species of the *Barosma.*

DIOSPHENOL $C_{10}H_{16}O_2$. [82°]. (c. 220°). The stearoptene in oil from buchu leaves (Spica, *G.* 15, 195; Shimoyana, *Ar. Ph.* [3] 26, 403). Monoclinic crystals (by sublimation); v. sol. alcohol, sl. sol. ether, insol. water. Smells like camphor. $FeCl_3$ gives a green colour.

Reactions.—1. Alcoholic KOH partly converts it into diolic acid $C_{10}H_{18}O_3$aq, which forms the following salts: BaA'_2 5aq. S. 1·5 at 17·5°; 5 at 100°.—AgA'.—2. Reduction in alcoholic solution by *sodium amalgam* forms $C_{10}H_{18}O_2$ [159°].—3. *Bromine* gives $C_{10}H_{14}Br_2O_2$ [43°].

Methyl derivative $C_{10}H_{15}MeO_2$. (234°). S.G. ^{15} ·985. From diosphenol, KOH, and MeI.

Ethyl derivative $C_{10}H_{15}EtO_2$. (271°). S.G. ^{15} ·967.

Acetyl derivative $C_{10}H_{15}AcO_2$. (270°). S.G. ^{20} ·1032.

DIPPEL'S OIL. An oil obtained by rectifying the oily product of the destructive distillation of bones or other animal matter. Recommended as a medicine by Dippel, an apothecary of the seventeenth century; *v.* BONE-OIL, vol. i. p. 522.

DISACRYL *v.* ACROLEÏN.

DISPOLINE $C_{11}H_{11}N$. (282°–304°). An alkaloid homologous with quinoline found among the products obtained by distilling cinchonine with potash (Greville-Williams, *Laboratory*, p. 109; *Z.* 1867, 428). Oil.—$B'_2H_2PtCl_6$. Not decomposed by boiling water (De Coninck, *Bl.* [2] 40, 271).

DISSOCIATION. A term proposed by Deville for the purpose of particularising a certain class of reactions chiefly studied by himself and by those whom he inspired.

Many facts now studied by the method of the theory of dissociation have been known from early days. The observations of Gay-Lussac on the decomposition of chalk by heat, and of Avogadro in 1811, and Ampère in 1814, on the abnormal vapour densities of gases may be mentioned. The starting-point of the modern doctrine is Grove's Bakerian Lecture (*T.* 1847), in which the decomposition of gases by heat, and especially the decomposition of water by fused platinum, is announced and explained. The following extracts will show that the theory of the decomposition of water was correctly stated by Grove, though the terms in which he expresses it are now obsolete. After describing the action of a hot platinum wire on dry and wet carbonic oxide respectively, he continues:—

> 'I thought much upon this experiment; it appeared to me ultimately that the ignited platinum had no specific effect in producing either composition or decomposition of

water, but that it simply rendered the chemical equilibrium unstable, and that the gases then restored themselves to a stable equilibrium according to the circumstances in which they were placed with regard to surrounding affinities; that if the state of mixed oxygen and hydrogen gas were, at a certain temperature, more stable than that of water, ignited platinum wire would decompose water as it does ammonia.' 'It now appeared to me that it was possible to effect the decomposition of water by ignited platinum; that, supposing the atmosphere of steam in the immediate vicinity of ignited platinum were decomposed, or the affinities of its constituents loosened, if there were any means of suddenly removing this atmosphere I might get the mixed gases; or secondly, if, as appeared by the last two experiments, quantity had any influence, that it might be possible so to divide the mixed gases by a quantity of neutral ingredient as to obtain them by subsequent separation (or as it were filtration) from the neutral substance. Both these were realised.'

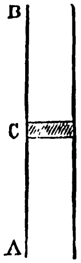
He then relates how on heating platinum in steam he got a small bubble of gas, which detonated when all was cold; and then says:—

> 'The experiment was then repeated, continuing the ignition for a longer time, but the gas could not be increased beyond a very limited quantity; indeed, it was not to be expected, as, supposing it to be a mixed gas, recombination of the excess would have taken place.'

The matter was taken up by Deville in 1857, who repeated Grove's experiments on a large scale. Advantage was taken of an old observation of Regnault concerning the action of molten silver on steam, and an equivalent method, in which silver is replaced by fused litharge, was described.

This is the first of the many ingenious methods invented by Deville for the study of dissociation-phenomena, and to him and his pupils we owe much of our knowledge on the subject. The appended bibliography (*v.* end of this article) will indicate the further history of the matter, as well as the more important memoirs which have appeared on the subject.

Before defining the meaning of the term *dissociation* it will be well to become in some measure acquainted with the simpler facts and arguments of the subject. Let A B be a tube made of some material capable of resisting a high temperature, such as glazed porcelain. Let C be a porous septum, *e.g.* a plate of porous earthenware, fitted into the tube A B, so as to be air-tight in the ordinary signification of the term. Let there be means of placing the end B of the tube in connexion with an air-pump and gas-analysis apparatus. The end A can be closed by a non-porous stopper, and the tube is to be so placed that it can be raised to any desired temperature. The space C A can be filled with any gas or vapour, and the stopper at A furnished with such arrangements as to allow the pressure of the vapour in C A to be kept constant, whatever the temperature may be. Though such a combination of apparatus as this has never been put together, and though it would be exceedingly inconvenient in practice, it is easy to understand, and will serve to establish the main principles of dissociation.



The part of the tube C A is supposed to be filled with saturated water-vapour, and is placed on the heating apparatus. B C is kept vacuous, or as nearly so as possible, by means of the air-pump. In now studying the changes produced in the water-vapour by the action of heat, let us direct our attention solely to the part of the tube C A. Then we know that, as the temperature increases from 100°, the dry steam in C A will expand at almost exactly the same rate as a permanent gas. In fact, if we made two air-thermometers at constant pressure, and filled one with dry air and one with unsaturated steam, they would keep together approximately till a very high temperature is attained – say, up to a red heat. After that we should observe that the expansion of the steam becomes greater than the expansion of air, and continues to increase, at all events up to the highest temperature we can reach experimentally. If we replaced the steam by the vapour of acetic acid, the same phenomena would be observed, except that we should finally be able to reach a point where the coefficient of expansion of the acetic acid vapour attained a maximum; and it would decrease from that point till it again became the same as for air. The apparatus with the porous plate will enable us to give an explanation of the change in the coefficient of expansion of dry steam. We know that when we mix two volumes of hydrogen and one volume of oxygen and keep the mixture at a temperature a little over 100°, and then explode the gases by means of an electric spark, so that they may form water-vapour, and finally allow the temperature to become the same after explosion as it was before explosion, then the three volumes will become reduced to two volumes. In other words, oxygen and hydrogen when combined together only occupy two-thirds of the space they occupy before combination.

Now, suppose that we heat the water-vapour, and let us *assume* that the heating in some way undoes the combination of the hydrogen and oxygen, so that we no longer have pure water-vapour, but a mixture of water-vapour, oxygen, and hydrogen. If we further *assume* that the ratio of the weight of the uncombined gases to the weight of the steam increases as the temperature rises, we shall have a hypothetical explanation of the change in the coefficient of expansion. This hypothetical explanation may be converted into a real explanation by experiments performed with the apparatus described. The *rate of diffusion* of different gases through porous septa is very nearly inversely proportional to the square roots of the densities of the gases. Hydrogen, therefore, passes through porous septa four times as fast as oxygen, and three times as fast as steam. If, therefore, the steam in the part of the tube A C be really decomposed, we shall be able to detect the decomposition by means of an analysis of the gases diffused into the part B C. In order to make the proof complete we must still show that no other change takes place in the steam in A C; this would be very difficult to do directly, especially for steam which only decomposes at very high temperatures, and therefore we must adopt a rather different method. If we can show that the change in the coefficient of expansion is proportional to the amount of steam decomposed at all temperatures, then we can deduce that the most important part of the change at all events is to be traced to the decomposition, or, as we shall say for the future, to the *dissociation*, of the steam. This may be done by means of our apparatus. Since the pressure in A C is kept constant, the 'partial pressure' produced by the hydrogen and oxygen will be proportional to the ratio of the weights of the uncombined gases to the weight of steam per unit volume. We know from experiment that the weights of gases diffused per unit time, under otherwise constant conditions, are proportional to the pressures, within the limit that the pressure is above some very small value depending on the kind of gas and the size of the pores in the septum. In all ordinary experiments the pressure is well above the limit. In order to simplify matters we will arrange our furnace so as to keep B C at the same temperature as A C, and let the air-pump work so fast that, however much gas comes through the plate, the vacuum is not perceptibly impaired. For a reason to be given further on, we will also allow the gas coming from B C to cool slowly, so that the hydrogen and oxygen may recombine. This will leave us with a mixture of water-vapour and hydrogen in our analysis apparatus. We have therefore to keep our diffusion-tube at different constant temperatures, allow the diffusion to go on slowly, and measure the amounts of hydrogen coming through per unit time. From what has been said, these quantities will be proportional to the dissociation at the temperature considered; and we have only to compare them with the coefficients of expansion at those temperatures to test our theory.

In no particular case does the evidence in favour of the hypothesis stated above amount to a complete demonstration. Thus in the case of bodies like sal-ammoniac, which decompose into substances chemically different from themselves, and therefore recognisable by chemical methods, no experiments have been made to show that the abnormal vapour density is *entirely* accounted for by the dissociation. Again, in the case of substances like nitrogen tetroxide and acetic acid, where the vapour-density is a function of the temperature, experiments have indeed shown that the quantities of heat absorbed at different temperatures, less the quantities of heat required to raise similar supposed less decomposable gases through the same range, are proportional to the rate at which the coefficient of expansion deviates from the normal. Unfortunately, in both these cases (the only ones specially studied as to this point) we have no chemical means of testing whether the supposed molecular decomposition takes place or not. In fact, some chemists consider it does not, but that we have in these cases merely a change comparable with that from the liquid to the gaseous state, and which does not take place at a definite temperature, but goes on gradually even though the liquid as such may have disappeared (v. Berthelot a. Ogier, *A. Ch.* [5] 36, 382). In other words, these chemists are inclined to attribute the change which takes place in the coefficient of expansion merely to the molecules of the gas increasing their mean distance from each other faster in these cases than in the standard cases. This view, however, would lead to a very serious modification of all our views as to the physical signification of the gaseous state. Avogadro's law would have to be abandoned amongst other things. On the other hand, if we consider that nitrogen tetroxide and acetic acid vapour suffer molecular decomposition, then we must allow that all other gases which are formed from their elements with condensation—like nitrous oxide, for instance—may also undergo a molecular decomposition, since their specific heats have small positive temperature-coefficients (Regnault). There is nothing surprising in this, in fact it is in complete accordance with the views of Clausius and Williamson and physicists generally on the meaning of the *definite composition of gases*. Ramsay and Young (*C. J.* 49, 790) have shown that the specific gravity of acetic acid vapour decreases as temperature rises, whether the pressure be large or small, and that the specific gravity also decreases as pressure falls, whether the temperature be high or low, but that the specific gravity of a normal vapour, such as that of alcohol or ether, increases as temperature falls until a limit is reached, after which the specific gravity remains unchanged.

The hypothesis of dissociation sketched above will therefore be adopted in what follows, for not only is it in complete harmony with every experimental fact observed, but it serves to coordinate and bring into the same field of view a very great number of experimental results, at first sight very unlike each other and inexplicable separately. It will be noticed that we have as yet said nothing as to the mechanism by which dissociation takes place; this is a very obscure subject, and indeed very often seems to depend, amongst other things, on the form and material of the containing vessel (Menschutkin a. Kanonalow).

The effect of porous surfaces, however, presents little difficulty to the kinetic, and still less to the vortex-ring, theory of gases. Practically it may be taken to mean that an experimenter attempting to reproduce any of the experiments described below will most probably fail to reproduce the numerical results unless he carefully copies the original experimenter's apparatus. Particular instances will be found in their proper places.

There is no reason to suppose that dissociation is limited to gases, or that a rise of temperature is the only physical condition capable of bringing it about. It is a matter of common experience that chalk, when heated, decomposes into quicklime and carbonic acid; and if the operation be conducted in a closed chamber so that the carbonic acid cannot escape, it is found that the decomposition of the chalk is never complete, and that recombination occurs, to a certain extent, when the temperature falls. There are many other substances which behave like chalk as far as their decomposition by heat is concerned; that is, their degree of decomposition in closed vessels is almost entirely a function of the temperature, and is reversible. The constitution of solutions of many salts in water or in other solvents also appears to be dependent on the temperature. All these phenomena are collected together as cases of *thermolysis*, or decomposition by heat alone, and their study forms the larger part of the subject of *dissociation*, which also embraces cases of decomposition by other physical processes, such as exposure to light or electrical discharges.

There are many substances which undergo a complete and non-reversible chemical change under the action of heat; these decompositions may be regarded as cases of unlimited dissociation, and are generally called decompositions simply. Such unlimited changes are, however, best studied by themselves, and will not be dwelt upon in this article. For convenience of treatment we may define dissociation as follows:—

Let there be a chemical system consisting of atoms of kinds, A, B, C, &c., capable of combining together in any way; and let their actual state of combination at any instant depend partially on the physical conditions to which the system is exposed at the instant considered; and let the state of combination be called the state y when the physical conditions are denoted by x. Then if y changes when x changes, in such a way that y always returns to its original value when x returns to its original value, the system is called a *dissociable system*. In fact the value of x must be independent of the 'previous history' of the system; this necessarily implies that in dissociable systems the change of state of combination must be reversible. Dissociation, therefore, is the doctrine of reversible chemical reactions. Dissociation-processes are but special cases coming under the general laws of chemical equilibrium; as such they will be considered in the article EQUILIBRIUM, CHEMICAL.

The changes which take place in the energy of the system as its chemical constitution varies must necessarily exert a very great influence on the readiness with which such variation can occur. It is obvious, for instance, that the state of combination cannot change by itself from a condition of less to a condition of greater energy unless that energy be supplied from without. A supply of energy has therefore to be provided in order that many dissociation reactions may take place. In consequence of this, the thermal changes taking place during some cases of dissociation have been carefully studied (Berthelot); and much valuable information has been drawn, in other cases, from a consideration of the available energy of the electric field (J. J. Thomson).

Before treating special cases in detail it will be well to form a simple working hypothesis of dissociation, in order to shorten, as much as possible, the treatment of the experimental results. Such an hypothesis is ready to hand if we translate the results of, say, our experiments on steam, into the language of the kinetic theory of gases, and the ordinary molecular and atomic theory of chemistry. Taking the case of steam, we may sum up the results arrived at by saying that as the temperature rises the kinetic energy of the molecules increases, and in consequence the number of molecular collisions per second, as well as the violence of these collisions, must also increase. When the atoms of oxygen and hydrogen are uncombined they will be called free atoms; when combined they will be called 'paired' atoms. The 'mean time' during which the atoms are free is called the 'mean free time,' and the time during which they are paired is called the 'mean paired time.' If in the case of a system of oxygen and hydrogen where we may have molecules of oxygen, hydrogen, and steam, as well as atoms of the two former, the actual state of combination at any instant will depend on the ratio of the paired to the free time. If the time during which the atoms of oxygen and hydrogen are paired together is long compared with the time during which they are free, or paired with atoms of the same kind as themselves, then we are considering what is equivalent to a volume of steam. If, however, the paired time is comparatively short, then the state of the system approximates more to that of a mixture of oxygen and hydrogen. If we assume that the ratio is altered by a variation of the frequency of collisions, or of their violence, or by any other variation produced by a rise of temperature, then we shall have increased decomposition if the ratio of paired time to free time decreases as the temperature increases. When the temperature falls, on the other hand, we shall get recombination.

We can, therefore, form a mental image of a purely mechanical character as to the way in which dissociation may take place. We should expect that the effects would be modified at the boundaries of the gaseous system; and that some of the phenomena observed might be traced to the influence of the state of the walls of the containing vessel; and so, in fact, it is. The presence of porous bodies in particular seems to exercise a profound influence on the chemical state of gaseous systems exposed to their action. The above hypothesis of the mechanics of dissociation is at present to be regarded as a mere hypothesis of the most arbitrary character: if we can justify it afterwards by cumulative evidence that is another matter.

It will also be convenient to take advantage of a very simple method of regarding the phenomena of dissociation first put forward by Pfaundler in 1867. We are to regard a system in which dissociation is taking place as a field in which two tendencies are at work; on the one hand a source of energy from without the system is tending to produce decomposition; and on the other the 'chemical nature' of the component parts of the system is tending to produce recombination. Without committing ourselves to explain in any way the *modus operandi* of these tendencies, we can see that it is possible for the system to attain a state such that the amount of decomposition and recombination per unit time is the same. When this state is reached the 'limit of the reaction' is said to be attained. If by raising the temperature of the system, or by any other means, we alter the potency of one of the tendencies, we shall have a new equilibrium or limit. The idea is that for every given set of conditions we shall have a definite equilibrium, which will alter when the conditions alter, and which is therefore called a 'mobile equilibrium.'

The ratio of the weight of the uncombined part of the system to the weight of the whole system which is capable of combination is called the 'fraction of dissociation,' and is a very convenient quantity in discussing dissociation phenomena. Thus in a system of hydriodic acid, weighing say 10 grams before dissociation takes place, we might arrive at a temperature such that 1 gram became decomposed; then the fraction of dissociation would be denoted by $\frac{1}{10}$, and would be expressed by the same number whether we added iodine or hydrogen in excess, or, indeed, any inert gas.

If the external conditions change, then a period of time, short or long, is required for a new equilibrium to be established. Different writers have adopted different methods of expression for the rate at which the new equilibrium tends to become established, and various arbitrary rules have been given for finding the velocity of the reaction, depending of course on special definitions of the expression 'velocity of reaction.' In some cases the velocity of the reaction has been defined as the weight of substances combined or decomposed per unit time in a system of arbitrarily chosen weight. The most exact method would be to define 'velocity' as the rate at which the fraction of dissociation changes. The particular definition which we may happen to adopt is not of any very great importance, since it is from a comparison of velocities, and not from their absolute value, that useful information is most readily obtained.

The object of experiment is to determine the relation existing between the fraction of dissociation, when the limit is attained, and the other quantities involved. The most important of these are temperature, pressure, and proportion of reacting substances. The velocities of the reactions must also be studied experimentally.

We follow Lemoine in his distinction between the reactions which take place in homogeneous systems, and those which occur in non-homogeneous systems. If we start with a homogeneous system and by dissociation convert it into a system which is not homogeneous, we should expect a corresponding modification in the reaction, and such is the case. The most valuable results will be obtained when the experimental conditions are as simple as possible; and therefore more attention ought to have been devoted to the dissociation of systems which remain homogeneous than to those which are non-homogeneous to start with, or which become so by dissociation. Unfortunately, however, it is difficult to experiment on homogeneous systems.

Qualitative experiments whereby the existence of the dissociation of compounds was established.—Regnault describes some experiments under the article '*Chaux*' (*Course élémentaire de Chimie* [1854], 2, 2,3,5) which show that some solid bodies, decomposable by heat into one or more solids and a gas, give off the gas more freely when in presence of a foreign gas than when exposed to the products of their own decomposition. Chalk loses its carbonic acid more freely in ordinary air than in an atmosphere of carbonic acid. Hydrated salts lose their water of hydration more readily in an atmosphere of dry air than in one of water vapour. Grove, as we have seen, demonstrated the decomposition of steam by heat, and pointed out that the condition that the decomposition shall be sensible is that the products of decomposition must be rapidly cooled, or in some other suitable way removed from the sphere of action before recombination can take place. From a theoretical point of view it is immaterial whether we hinder recombination by preventing the atoms from getting to one another through admixture with an inert gas, or whether we lower the temperature so rapidly that it falls below the combination point before all the atoms are recombined.

Deville first laid down these principles with great clearness, and practically invented all the apparatus requisite for the realisation in practice and on a large scale of the necessary conditions. His apparatus is of three kinds.

I. For raising gases to a high temperature, and removing, at that temperature, the products of dissociation, by taking advantage of the laws of gaseous diffusion.

II. For raising gases to a high temperature and preventing recombination by admixture with an inert gas.

III. For raising gases to a high temperature and preventing recombination by sudden cooling. This apparatus took two forms:—

α The hot and cold tube.

β Apparatus for sucking the hot gases into a tube through which water is circulating.

Exact information may be obtained from Deville's papers (*v.* Bibliography); and especially from his *Leçons sur la Dissociation professée en* 1864 *devant la Société Chimique.*

I. A glazed porcelain tube is fitted with good corks at each end; through these corks, and concentric with the axis of the porcelain tube, another tube of unglazed earthenware is passed. The porcelain tube can be heated, by means of a suitable furnace, to a very high temperature. The gas to be decomposed is made to circulate through the annular space between the two tubes. A current of an inert gas continually passes through the tube of unglazed earthenware and sweeps away with it the products of diffusion (*v.* fig. 1).

Deville decomposed steam by means of this apparatus, using carbon dioxide as the inert gas; the carbon dioxide was subsequently absorbed by potash, leaving a mixture of oxygen and hydrogen.

II. A porcelain tube is filled with pieces of porcelain in order to expose a large surface. The gas to be decomposed is mixed with a much larger volume of some inert gas and passed through the tube which is heated as before. This apparatus is not so powerful as the one last described. In an experiment in which a mixture of steam and carbon dioxide was passed through the apparatus, the yield of explosive mixture of oxygen and hydrogen was much smaller than when the porous tube was used; though of course in that case the mixture was chiefly hydrogen. This method is less applicable to quantitative experiments because of the complication introduced by the action of the large extent of porcelain surface exposed.

III*a*. *The hot and cold tube*: this was used first for demonstrating the decomposition of carbonic oxide into carbon and carbon dioxide. It resembles form I. with the modification that the porous central tube is replaced by a tube of silver through which a stream of cold water is kept constantly flowing. The decomposition of the carbonic oxide gas was proved by the deposition of carbon on the silvered tube, and by the presence of carbon dioxide in the stream of gas which passed through the tube.

III*β*. An apparatus of the same kind as the last, but with the important modification that a small hole of ·2 mm. diameter is bored in the side of the metal tube. The result is that when a stream of water is allowed to flow through the tube, air is sucked in at the small hole after the manner of a velocity pump. This apparatus was employed by Deville to examine the constitution of the gases in the middle of a candle flame; and was afterwards employed by Cailletet for extracting the gases from a blast furnace (*C. R.* 62, 891).

By means of these various forms of apparatus the dissociation of the following gases was demonstrated:—

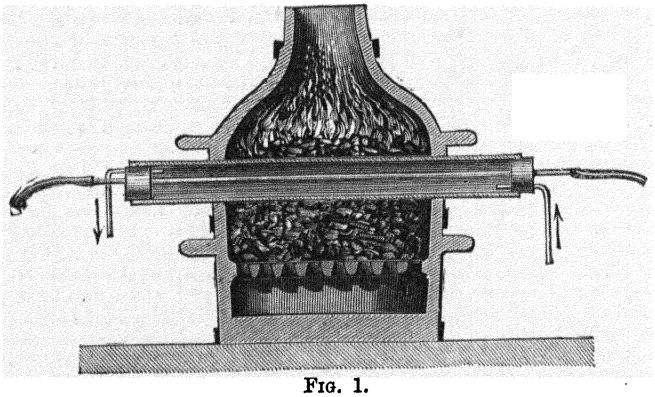
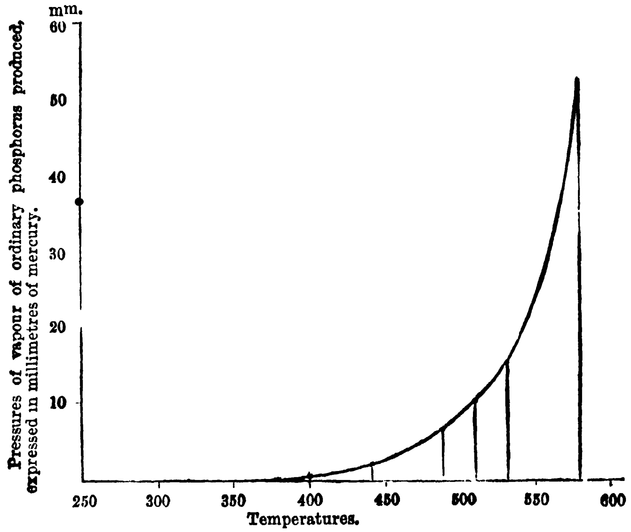


FIG. 1.

Water vapour by I. and II.—Carbon dioxide by II.—Carbonic oxide by III.; carbon deposited on the tube.—Sulphur dioxide by III.; tube blackened, and deposit of sulphur trioxide on it.—Hydrochloric acid by III.; surface of tube being previously amalgamated, and chloride of mercury and silver formed by the dissociation.

It will also be convenient to notice here the dissociation of gases produced by electrical discharge. There is no real difference between the spark discharge and the so-called silent discharge. The silent discharge is merely a spark discharge in which the sparks are very numerous and very small. In the cases where a limit has not been observed, the explanation is to be found in the fact that one or more of the products of decomposition is either liquid or solid, and is so removed from the sphere of action. This is notoriously the case with acetylene and hydrocarbons generally. Where a limit is attained, the reaction may generally be made complete by introducing a substance capable of absorbing at least one of the products of decomposition. It was formerly believed that the decomposition of gases by electric sparks was, so to speak, merely an accidental phenomenon connected with the rapid heating and cooling of portions of the gas. J. J. Thomson (*P. M.*, June 1883) has, however, given good reason for believing that decomposition is a necessary condition for the passage of electrical discharges; that in fact a spark can no more pass through an atmosphere of water-vapour without resolving it partially into oxygen and hydrogen than an electric current can pass through copper sulphate solution without decomposing it into copper and sulphuric acid. Whether Faraday's law of electrolysis extends to gases is still an open question; the probability is that it does not. However the decomposition is produced, there will probably be a certain amount of recombination as soon as the gases cool sufficiently. Since the products of decomposition are in general diluted with a large proportion of undecomposed gas, the temperature of the decomposed portions will often fall below the minimum temperature of combination before complete recombination has had time to take place. This will leave a balance of decomposition at each spark. As soon, however, as the products of decomposition have accumulated to a small extent, they, as well as the undecomposed gas, will be acted on by the spark, and a certain amount of recombination will take place. It must be noted, however, that the decomposition produced by each spark is very small, since the energy of the electric field is in general small compared with the amount of energy required to produce even a small decomposition. After a certain length of time the decompositions and recombinations will become equal, and the limit of the reaction will be attained. The production of a limit in the experiment of ozonising oxygen is well known, and the production of ozone at all shows that oxygen molecules must be previously electrolysed into oxygen atoms. This is also proved by an experiment of De la Rue and Müller, repeated and modified by Thomson and Threlfall, whereby a large increase of volume is observed to take place in a tube through which a spark passes, and which is much greater than can be accounted for by the expansion due to heating. In oxygen, if the sparks are very small so that the heating is insignificant, a diminution of volume is observed to take place owing to the production of ozone The action of the spark on gases seems to be dependent on the nature of the spark, and this in turn depends to a great extent on the pressure of the gas. Much work still requires to be done in this direction. At present the following list of gases which have been decomposed will suffice: Oxygen, nitrogen (?), carbon dioxide, methane, ether, acetylene, ammonia, acetic acid, phosphoretted hydrogen, carbonic oxide, hydrocarbons generally, sulphuretted hydrogen, seleniuretted hydrogen, cyanogen, &c. Decomposition of the fluorides of boron and silicon and chlorine has not yet been observed, but there is little doubt that the decomposition of these bodies will ultimately be demonstrated. Most of the above observations have been made by P. and A. Thénard (*C. R.*) and by Berthelot An account of the extremely valuable researches of Berthelot and Vieille on dissociation during explosion, as well as of the observations of Dixon, will be found in the article EXPLOSION.

Curve representing the pressures of ordinary phosphorus which limit the allotropic transformation of the phosphorus at different temperatures.



Scales: 1 mm. for 1 mm. of vapour-pressure, and 0·2 mm. for 1 degree of temperature.

FIG. 2.

Quantitative Experiments on Dissociation.—It is now our business to discuss the quantitative experiments which have been made on particular cases of dissociation. From a theoretical point of view these experiments fall into two classes:

(α) *Those made on the determination of the limit, and its dependence on pressure, temperature, &c.*

(β) *Those referring to the velocity of the reaction.*

From an experimental point of view very different methods have to be adopted in different cases. In one class of experiments the observations take the form of determinations of vapour density at different temperatures and pressures. Experiments on velocity usually depend on the ordinary methods of analysis; and of course involve observations by the chronometer. In many cases observations of high temperatures have to be made, and these are subject to the almost unavoidable experimental uncertainty attendant on that very difficult operation. A judgment as to the trustworthiness of the results obtained can in general be formed only from a study of the observer's own account of his experiments.

The methods of thermal chemistry have been applied by Berthelot to the solution of many interesting questions.

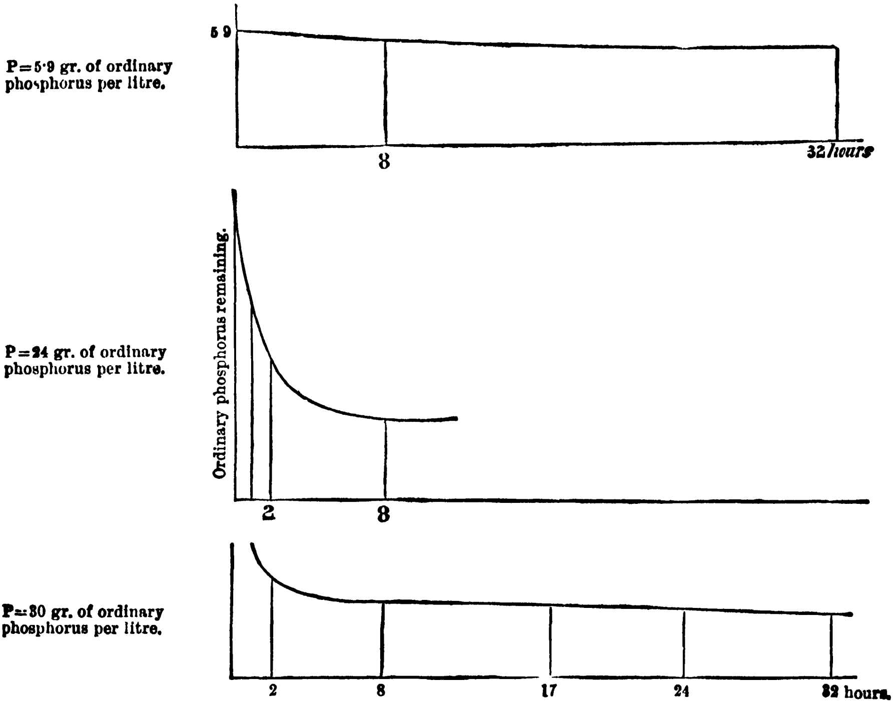
Dissociation in non-homogeneous systems.—We shall consider first the allotropic change produced by heat in ordinary phosphorus. When yellow phosphorus is heated in a closed space it is partially changed into red phosphorus; and when red phosphorus is heated it is partially converted into yellow phosphorus. It is found that neither reaction is complete, but that the same limit is attained whether we start from red or from yellow phosphorus. If we start with yellow phosphorus, and heat it to a definite temperature in a closed vessel in connexion with a manometer, a transformation into red phosphorus will take place. Yellow phosphorus has a considerable vapour-pressure; the transformation will go on till the pressure inside the vessel reaches a certain value; this value will be less than the maximum vapour-pressure of red phosphorus corresponding to the temperature, and is called the 'limiting pressure.' If, on the other hand, we start with red phosphorus, the vapour-pressure will diminish from the maximum to the limiting pressure. This pressure is found to be the same in both cases, provided the temperature is the same. Analysis of the residue gives the proportions of red and yellow phosphorus. Each temperature has its definite limiting pressure. If we start with a small quantity of yellow phosphorus, and heat it in a vessel so large that it is not able to produce the limiting pressure corresponding to the temperature, no red phosphorus will be formed. The phenomenon is, therefore, quite analogous to the vapourisation of a liquid according to the two cases when the conditions are such that the vapour is (*a*) saturated, or (*β*) unsaturated.

The accompanying curves (figs. 2, 3, 4) and numbers will give the results obtained. (The results are chiefly taken from Lemoine's *Études sur les Équilibres Chimiques.*)

Ordinary phosphorus introduced into a space of one litre.	Quantities of ordinary phosphorus persisting at 440° at the end of:							
	5m.	¾h.	2h.	8h.	17h.	24h.	32h.	41h.
Grams.	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.
2·9 (Lemoine)	—	—	—	2·9	—	—	—	—
5·9 *id.*	—	—	—	5·3	—	—	4·9	4·7
16·0 *id.*	—	—	—	5·0	—	—	—	—
24·0 (Hittorf)	15·5	11·1	7·0	4·4	—	—	—	—
30·5 (Lemoine)	—	—	5·4	4·0	3·7	3·6	—	—

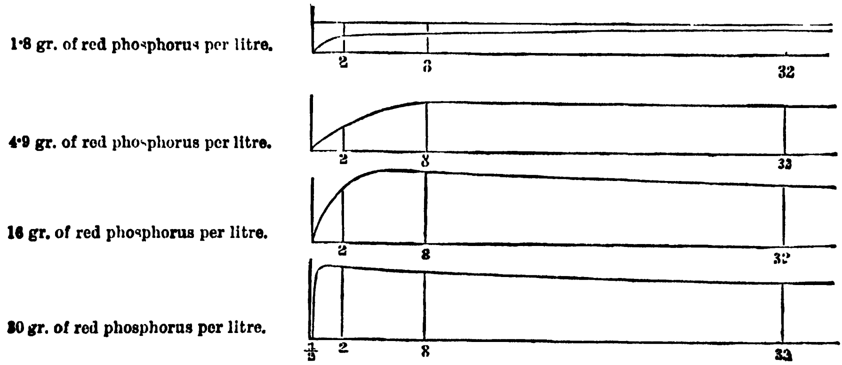
The common limit is 3·6 grm.

Curves representing the weights of ordinary phosphorus remaining at the end of different times, for a similar weight P of ordinary phosphorus introduced (Lemoine).



Scales : 2½ mm. for 1 hour, and 2½ mm. for 1 gram.

FIG. 3.



Scales : 2½ mm. for 1 hour, and 2 mm. for 1 gram.

FIG. 4.

We may account for these same differences by calculating, according to the preceding data, the mean quantity of red phosphorus produced in one hour:—

Ordinary phosphorus introduced per litre.	Red phosphorus formed in grams in one hour at 440°. Time. from 0 to 2h.	from 2 to 8h.	from 8 to 32h.
grms.			
5·9	← 0·075 →		0·015
30·0	12·30	0·233	0·015

Temperature 440°.

Red phosphorus employed per litre.	Quantities of ordinary phosphorus in grams produced at the end of: ½h.	2h.	8h.	23h.	32h.	39h.	47h.	83h.
1·8 . . .	—	0·80	1·33	—	—	1·7	—	—
4·9 . . .	—	1·62	2·9	—	—	3·3	—	3·32
16 . . .	—	3·67	4·6	—	4·0	—	—	—
30 . . .	4·54	4·75	4·4	3·9	3·71	—	3·72	—
100 . . .	—	—	4·2	—	—	—	—	—
1000 . . .	—	—	3·5?	—	—	—	—	—

It will be noticed that in some of the velocity experiments, starting from red phosphorus, the vapour-pressure at first produced is higher than the pressure of the limit; this is explained by the previous history of the red phosphorus, of which it appears there are several allotropic modifications depending on the temperature at which they have been produced. This has been studied by Troost and Hautefeuille and completely explained.

Cyanogen is slowly transformed into paracyanogen on heating. The velocity is very small, but appears to be greatest at about 500°. The inverse reaction has a comparatively great velocity. There is a limiting pressure of transformation just as in the case of phosphorus. Observations are complicated by a continual slow decomposition of the cyanogen into nitrogen and carbon. An analysis has, therefore, to be made of the residue before the correct limiting pressure can be obtained. The following are the numbers of Troost and Hautefeuille:

Temperatures	Pressures of the cyanogen in mm.
502°	54
506	56
559	123*
575	129*
587	157
599	275*
601	318
629	868*
640	1310

The numbers with asterisks have been obtained with paracyanogen prepared from cyanide of silver. The others have been furnished by paracyanogen prepared from cyanide of mercury, and perfectly freed from the metal.

Cyanic acid is converted into cyamelide and *vice versâ*. The velocity depends on the temperature; and it is by no means the same for the two reactions. A complication is introduced, because above 150° gaseous cyanic acid is transformed into solid cyanic acid; and below 150° cyamelide is produced. The production of a maximum vapour-pressure limiting the decompositions is perfectly clear and definite. The numbers are—

Temperatures	160°	170	180	195	215	227	251	330	350
Transformation-pressures	56mm.	68	94	125	157	180	285	740	1200

Allotropic transformations of homogeneous systems. *Acetic acid.* The vapour of acetic acid has long been known to possess a vapour density greater than the theoretical density. This diminishes, however, as the temperature rises, or, in other words, the coefficient of expansion of acetic acid vapour between certain temperatures is greater than it is for most gases. A discussion of the explanations advanced to account for this has been already given. The data for the dissociation of acetic acid are given on p. 394 (Ramsay a. Young, *C. J.* 49, 790).

Nitrogen tetroxide (Deville and Troost, *C. R.* 64, 237). The relation between the vapour-density and temperature of nitrogen tetroxide under ordinary pressures shows that at about 150° the change of tetroxide into a gas of the molecular formula NO_2 is complete. The numbers are as follows:—

Dissociation of nitrogen tetroxide N_2O_4. Sp. gr. of $N_2O_4 = 3{\cdot}18$; of $NO_2 + NO_2 = 1{\cdot}59$; (air = 1).

Temp.	Sp. gr. of gas	Percentage dissociation	Mean increase in percentage dissociation for 10° rise of temperature
26·7°	2·65	19·96	6·5
35·4°	2·53	25·65	8·1
39·8°	2·46	29·23	11·0
49·6°	2·27	40·04	12·1
60·2°	2·08	52·84	13
70°	1·92	65·57	10·4
80·6°	1·80	76·61	8·8
90°	1·72	84·83	4·4
100·1°	1·68	89·23	3·1
111·3°	1·65	92·67	3·5
121·5°	1·62	96·23	1·8
135°	1·60	98·69	
154°	1·58	100	

Troost, continuing the experiments in 1878 at very low pressures, finds that at temperatures as low as 27° complete dissociation may take place.

Naumann gives a large series of numbers, as in the case of acetic acid vapour, between temperatures of −6° and +22·5° and pressures of 84 to 301 mm. Another determination of the density of nitrogen tetroxide vapour has been made with extreme care by E. and L. Natanson (*W. A.* 1886. 164).

As has been already stated, Berthelot and Ogier have measured the specific heat of acetic acid and nitrogen tetroxide vapours. The method adopted was Regnault's; care was taken in the case of nitrogen tetroxide to have all the apparatus made of glass. The specific heats were of course measured under constant pressure. Through the range of temperature over which it undergoes change, the specific heat is enormously greater than the mean specific heat of permanent gases formed from their elements with condensation. For the latter Regnault gives, for nitrous oxide, for instance;

Molecular specific heat $8{\cdot}76 + {\cdot}0055t$
And for carbon dioxide $8{\cdot}23 + {\cdot}01177t$,

while for gases formed without condensation we have practically the same value without a temperature-coefficient, at least up to 200°. For some organic substances the specific heats are much greater. Wiedemann gives as follows:—

	Molecular specific heat
Ethyl bromide	$14{\cdot}76 + {\cdot}0388t$
Acetic ether . . .	$24{\cdot}1 + {\cdot}0765t$
Benzene	$17{\cdot}45 + {\cdot}0798t$,

while for acetic acid and nitrogen tetroxide the specific heat rises above 50°, and the temperature-coefficient is itself a function of the temperature. The following numbers will make the results of Berthelot and Ogier clear:—

Temperature interval	Total heat absorbed by 1 gram-molecule of N_2O_4 expressed in gram-degrees	Mean molecular specific heat for the range specified
27° to 67° (40 degrees)	2988·0	74·7
67° „ 103° (36 „)	2050·8	57·0
103° „ 150° (47 „)	1271·1	27·0
150° „ 198° (48 „)	436·1	9·1
198° „ 253° (55 „)	463·4	8·9
253° „ 289° (36 „)	594·2	12·9

This table shows that the heat absorbed is very great, even at 27°, and the specific heat diminishes till the temperature of 150° is reached. From there it remains fairly constant till the temperature rises to 253°, and above that it increases. Berthelot subtracts from the values given above, the heat which would be taken to raise the temperature of a non-dissociable gas through the same ranges, adopting Regnault's formula, molec.sp. heat $= 8{\cdot}76 + {\cdot}0055t$. The remaining heat is probably taken up in dissociation-work; assuming this to be the case, Berthelot calculates the amount of dissociation which should take place, and compares the result with the numbers obtained by Naumann and Salet as deduced from observations on the vapour density. It will be seen that the numbers agree as well as could possibly be expected, bearing in mind the unavoidable experimental errors of such a difficult operation as a determination of the specific heat of a gas.

Decomposition between different temperatures as deduced from heat absorbed		Decomposition between different temperatures deduced by Naumann and Salet from vapour density observation	
Range of temperature	Decomposition in percentages of total	Range of temperature	Decomposition in percentages of total
27° to 67°	40	Below 26°	20
67° „ 103°	26·3	26° to 70°	35·6
103° „ 150°	13·2	70° „ 100°	23·6
		100° „ 136°	9·5
	79·5		68·7

The agreement will be better seen from the curve (fig. 5). In order to compare the two effects the ordinates are proportional to the quantities of heat absorbed for one curve, and proportional to the decomposition in the other. The abscissæ give the temperatures. It will be seen that the agreement is very close; if it were complete the curves would coincide. It is still closer, however, for acetic acid vapour, for which Berthelot and Ogier have made similar experiments and calculations. The curves will explain this; for the actual numbers *v.* the original paper. An extension of Gibbs' thermo-dynamic theory has been made to embrace these variations of specific heat by Duhem (*J. de Ph.*, July 1886). The calculated and observed variations seem to agree fairly well.

Iodine.—The vapour-density of iodine varies with temperature and pressure. A very full and complete study by Crafts and Meier has been made of the vapour of iodine (*v.* curves, fig. 6). The results may be summarised by saying that from 300° to 700° iodine vapour behaves like a perfect gas; at 700° the relative density of the vapour begins to diminish under all pressures, and this continues till the temperature reaches a value of about 1,500°, when the vapour again conforms to the gaseous laws. The two states, below c. 700° and above 1,500°, correspond to the

Acetic acid. Theoretical vapour-density (H = 1) 29·92.

Pressure in mm.

Temp.	20	40	100	300	500	1000	2000	5000	10000	16000	20000	24000
40°	54·22											
50°	50·62	53·61										
60°	47·04	50·38										
70°	43·55	47·12	51·21									
80°	40·45	43·86	48·08									
100°	35·63	37·92	41·81	48·50								
120°	32·75	34·01	36·50	42·79	46·71							
140°	31·32	32·12	33·72	38·05	41·42	46·81						
160°			32·10	34·77	36·88	41·80	47·81					
180°			31·17	32·66	34·01	37·39	42·58					
200°							38·64	47·99				
220°							35·82	42·39				
240°							34·00	38·79	47·60			
260°							32·89	36·39	42·80	53·00		
280°							32·21	34·66	39·10	45·45	51·34	60·70

formulæ I_2 and I respectively. Considering the rate of dissociation and its relation to pressure we may say that the rate of dissociation per degree of temperature becomes greater as the pressure diminishes. These changes are accompanied by a change of the absorption-spectrum (Salet, *Bl.* 1873. 674).

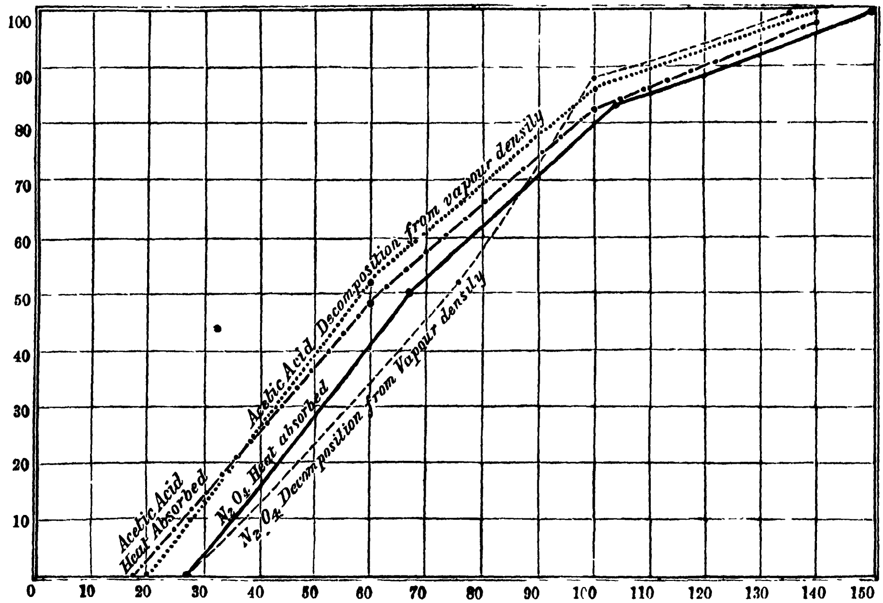
Dissociation of compounds.

I. ***Systems that are not homogeneous.***

Carbonate of calcium.

Bibliography.—Debray (*C. R.* 64, 603); Weinhold (*P.* 149; *J.* 1874. 119); Raoult (*C. R.* 1881. 189); Birnbaum and Maher (*Bl.* 1880. 88); Wiedemann (*P. Jubelbd.* 1874. 474; *J. pr.* [2] 9, 338).

Debray made the first research on this subject. His method consisted in heating Iceland spar in a vessel connected with a manometer and air-pump; an arrangement providing for the introduction of carbon deoxide was also attached to the apparatus. Decomposition of the calcium carbonate begins at 440°, the crystals becoming opaque owing to changes at the surface. Above this point the phenomenon of limiting pressure depending on the temperature is observed. According to Debray the limit is the same whether we start from calcium carbonate in a vacuum, or from quicklime in an atmosphere of carbon dioxide. If in any case the pressure is kept below the limiting pressure corresponding to the temperature, the Iceland spar will be completely decomposed.



For the acetic acid curves the temperature scale is supposed to be increased by 100°. The heat absorbed between 120° and 250° is divided into 100 parts, as is the change of vapour-density.

For the nitrogen tetroxide the amount of heat absorbed between 127° to 198° is divided into 100 parts, as is the dissociation as given by Naumann and Salet.

FIG. 5.

Vapour-pressure at 860° = 85 mm. of mercury.
" 1040° = 520 mm. "

Weinhold, repeating these experiments, finds that the pressure of CO_2 is always greater than Debray found it, and that the variations of pressure are never regular. Raoult finds that, starting with quicklime and CO_2, combination takes place with incandescence at about 550°. The compound formed has, however, the formula $(CaO)_2CO_2$. This compound is capable of absorbing more carbon dioxide, though the velocity of the reaction is very small; in twelve hours after a continual passage of a stream of CO_2 over the compound, analysis shows that a body of the composition $4CaO.3CO_2$ is produced, and an extremely slow absorption still goes on. Raoult also finds that the amount of carbon dioxide absorbed depends on the previous history of the quicklime and that it is much less absorbent if it has been previously heated to a high temperature. Wiedemann finds that much depends on the crystals of Iceland spar selected being previously carefully dried. Debray is probably substantially correct in his general deductions, but not in his experiments.

Hydrated salts.—Efflorescence (Debray, *C. R.* 1868. 194). In general, the same phenomena are observed in heating hydrated salts as in heating calcium carbonate. There is a definite limiting pressure for every temperature; this is the same whether the water-vapour exists by itself or in presence of air. In fact the hydrated salts act very much like liquids in their appreciation of 'partial pressures.' The phenomena are modified in accordance with the fact that each salt is generally capable of forming more than one definite hydrate.

The numbers observed by Debray for crystallised sodium hydrogen phosphate will serve as examples. $(Na_2HPO_4 + 24H_2O)$ and

($Na_2HPO_4 + 14H_2O$). f is maximum vapour-pressure of the salt, F is pressure of water-vapour at same temperature:—

Temperatures	Phosphate of sodium containing from 14 to 24 H_2O		Phosphate of sodium containing a little less than $14H_2O$	
	f	$\frac{f}{F}$	f	$\frac{f}{F}$
°	*millimetres*		*millimetres*	
12·3	7·4	0·694	4·8	0·452
16·3	9·9	0·717	6·9	0·500
20·7	14·1	0·776	9·4	0·517
24·9	18·2	0·777	12·9	0·551
31·5	30·2	0·819	21·3	0·618
36·4 (the salt melted)	39·5	0·877	30·5	0·678
40·0	50·0	0·901	41·2	0·750

Wiedemann has observed the relation between limiting pressure and temperature for the following salts:—

$MgSO_4.7H_2O$

Temp. °	Pressures mm.	Temp. °	Pressures mm.
24·3	17·8	50	75·7
35	35·6	60	122·5
40	47·2	70·4	190·3
40·2	46·3	80	276

$ZnSO_4.7H_2O$
(The crystals melt at 70·5°)

Temp. °	Pressures mm.	Temp. °	Pressures mm.
16·5	113·9	60	116·6
30	20·3	70	170·8
40	44·2	75	221·2
40	43·6	85·5	376·4
50	73·1	90	427
50	74·5		

$CoSO_4.7H_2O$

Temp. °	Pressures mm.	Temp. °	Pressures mm.
22·1	115·9	65	168·2
35	34·6	75	252·6
35	35·6	75	254·7
45	62·3	85	377·4
45	65	90	447·9
55	106		

$NiSO_4.7H_2O$

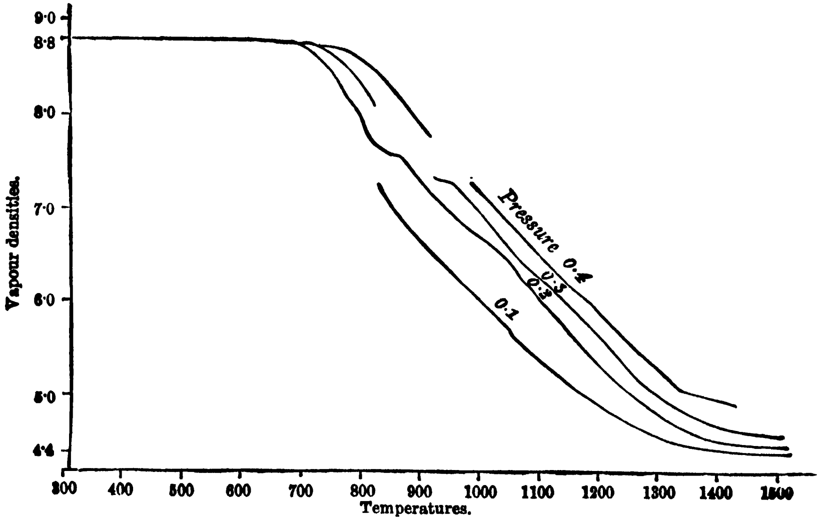
Temp. °	Pressures mm.	Temp. °	Pressures mm.
25	19·3	65	163·8
35	36·4	65	165·9
35	38·4	75	251·6
45	63·7	83	342·5
55	105·6		

Sulphate of iron $FeSO_4.7H_2O$
(The crystals melt at about 90°)

Temp. °	Pressures mm.	Temp. °	Pressures mm.
20	10·9	65	163·4
30	20·3	65	160·9
40·2	40·1	75	263·9
50	74·8	86	397·7
55·2	103·5	93·5	548·9
60	131·3		

Naumann has studied the efflorescence of sulphate of copper very carefully, and it is chiefly through his researches that the influence of previous history and the precautions necessary in observing the equilibrium of slow velocity changes have been brought to light. These experiments show very clearly how the velocity depends on the state of the salt with respect to the size of its particles. In the case of crystals a slow progressive change goes on as the inner portions become dehydrated, and it is only when

Curve representing the density of iodine vapour at different temperatures and at different pressures according to the experiments of Crafts and Meier (Lemoine).



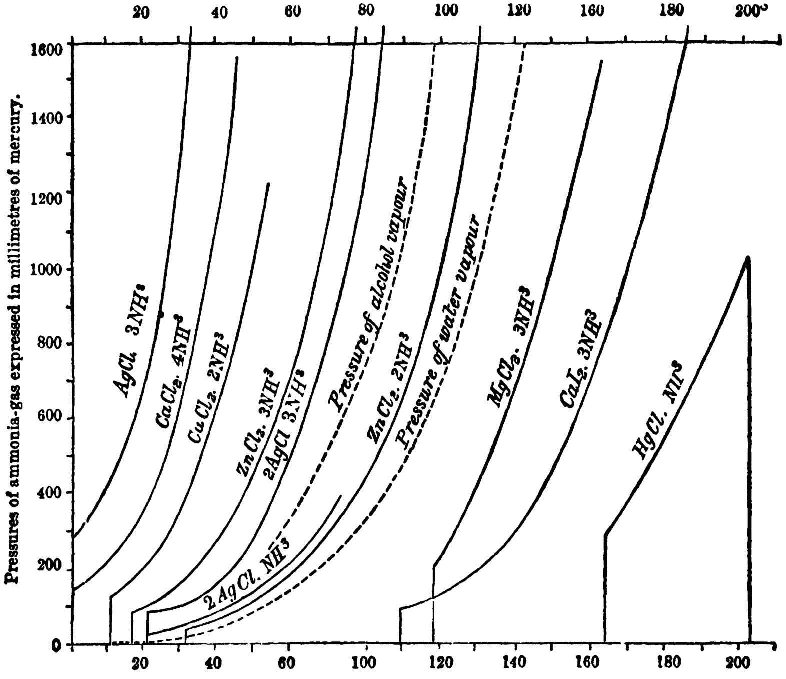
Scales: 8 mm. to 100 degrees, 12·25 mm. to 1·0 of variation of density.

Fig. 6.

the composition of the crystals is uniform throughout that the equilibrium is obtained.

Carbonates of manganese and silver (Joulin, *A. Ch.* 1873. 276).—The velocity of the reaction is very slow; and the influence of the previous history is even more marked than in the case of carbonate of lime, so much so that the author considers that allotropic modifications of the salts exist, and that these have different vapour pressures. Carbonate of silver appears to be even more irregular in its behaviour than carbonate of manganese. Lemoine has summed up these experiments as follows. After laying down the simple principles as deduced from experiments on carbonate of lime he says: 'Mais il peut se présenter des cas où la combinaison, tout en se faisant en même temps que la décomposition, soit si lente que toutes sortes de circonstances accidentelles influent sur elle: il peut se faire que les éléments mis en liberté éprouvent des modifications allotropiques, au moins commençantes, qui gênent leur combinaison nouvelle. Dans tous ces cas, l'établissement d'une tension limite, tout en étant l'expression générale du phénomène, se manifestera moins nettement, parce que la loi est compliquée par différentes circonstances accessoires.'

Curves representing the pressures of ammonia-gas which limit the dissociations of ammoniacal chlorides at different temperatures.



Scales: 0·5 mm. for 1 degree of temperature, and 5·0 mm. for 100 mm. of pressure.

FIG. 7.

Mercuric oxide (Myers, *Bl.* 1871).—The experiments are so complicated by the vapour of mercury set free that no useful information has yet been drawn from them.

Oxide of iridium (H. St. C. Deville and Debray, *C. R.* 1878. 441).—A clear example of dissociation. Limit at 823° is 5 mm., and at 1139°, 745 mm. At 1000° the limiting pressure is greater than the partial pressure of oxygen in the air at atmospheric pressure; it follows from this that at temperatures below 1000° the iridium oxide can decompose in air, and at temperatures above this iridium is non-oxidisable.

Compounds of metallic chlorides with ammonia, studied by Isambert (*C. R.* 1878).—The curves (taken from Lemoine) will suffice to explain the matter sufficiently (fig. 7).

Chloride of sulphur, and the compound formed by the combination of cuprous chloride and carbonic oxide, appear to dissociate, and have given rise to some discussion (Berthelot, *A. Ch.* [3] 46, 48; Michaelis, *A.* 170; Isambert, *C. R.* 1878).

Metallic hydrides (Troost a. Hautefeuille, *C. R.* 1874 a. 1875).—These researches have shown that hydrogen may be associated with metals in three different ways:—1. By simple condensation as in the well-known case of platinum black. 2. By solution. 3. By chemical combination. Heating the substance in a closed space in connexion with a manometer and air-pump will at once show which of the three forms of combination is exhibited in any special instance. If the gas is simply condensed there will be no definite relation between the pressure and the temperature. It generally happens that the second and third order of phenomena are exhibited together. In this case the gas that is dissolved will be simply evolved on heating, and will leave a more or less definite compound having a definite limiting dissociation pressure.

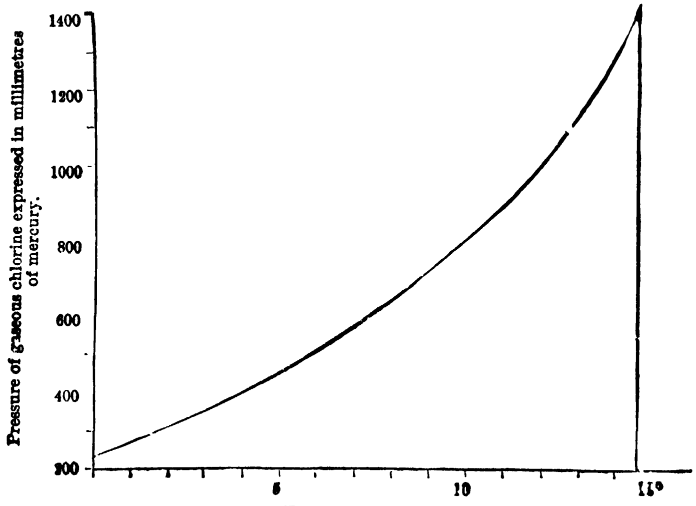
For instance, *potassium hydride* K_2H 'dissolves' forty times its volume of hydrogen, so that on heating and exhausting this gas is evolved. It would probably, however, be more accurate to say that two or more hydrides may be formed of different degrees of stability. On raising the temperature we get a definite dissociation of the potassium hydride which remains. The numbers are:—

Temperatures °	Pressures of dissociation mm.	Temperatures °	Pressures of dissociation mm.
330	45	390	363
340	58	400	548
350	72	410	736
360	98	420	916
370	122	430	1,100
380	200		

And for *sodium hydride*, in which hydrogen is much less soluble, the numbers are:—

Temperatures °	Pressures of dissociation mm.	Temperatures °	Pressures of dissociation mm.
330	28	390	284
340	40	400	447
350	57	410	598
360	75	420	752
370	100	430	910
380	150		

Dissociation of chlorine hydrate.



Scales: 5 mm. for one degree of temperature, 5 mm. for 100 mm. of pressure.

FIG. 8.

Palladium hydride gives:

Temperatures °	Pressures of dissociation mm.	Temperatures °	Pressures of dissociation mm.
20	10	120	467
40	25	140	812
60	50	160	1,475
80	106	170	1,840
100	232		

The *compound formed by chlorine and water* dissociates very readily, giving the curve shown in fig. 8.

Hydrogen selenide.—The dissociation of this gas has been studied by Ditte (*C. R.* 1872. 980). It apparently presents the extraordinary anomaly of the dissociation-pressure not increasing continuously with the temperature. It must be noted, however, that below the temperature of 270° the velocity of the reaction is so small that the composition of the gaseous mixture has to be determined by a sudden cooling of the sealed tubes containing the gas, and a subsequent analysis of their contents. It may be very fairly asked how, in the first place, this procedure gets over the velocity difficulty, and, in the second place, whether it is likely to give any information at all seeing that no cooling can take place in an infinitely short time. The following numbers will give an idea of the velocity of the reaction when selenion is heated with hydrogen:—

Temperature of 350°.

Number of hours	Proportion per 100 of H_2Se formed	Number of hours	Proportion per 100 of H_2Se formed
10	31·4	63	37·8
24	33·1	74	37
25	34·3	96	37·8
44	36·6		

Temperature of 440°.

Number of hours	Proportion per 100 of H_2Se formed	Number of hours	Proportion per 100 of H_2Se formed
15	45·3	69	50·6
21	48·8	165	51·5

The effect on the velocity of changing the pressure of the hydrogen is small, and acts so as to diminish the velocity when the pressure increases; but the limit of the reaction was probably never attained in these experiments. The effect of porous bodies has also been studied by Ditte, and the result is that a small but definite increase of velocity is due to their action, which is less marked, however, at high than at low temperatures.

Ammonia and carbon dioxide (Naumann, *A.* 84; Horstmann, *A.* 1887).—The limiting pressures of dissociation of ammonium carbamate are given by Naumann as follows:—

Temperatures °	Pressures of dissociation mm.	Temperatures °	Pressures of dissociation mm.
−15	2·6	26	97·5
−10	4·8	30	124
− 5	7·5	36	191
0	12·4	40	248
6	22	46	354
10	29·8	50	470
16	46·5	55	600
20	62·4	60	700

The velocity is small and increases with the temperature; it also largely depends on the extent of surface exposed by the carbamate.

Naumann and Horstmann have studied the effect of the presence of an excess of ammonia or carbon dioxide. They find that the effect of an excess of either gas is to hinder the dissociation. In other words, the limiting pressure is diminished by the presence of an excess of either gas. This does not appear to be the same for the same excess of either gas. With a given excess the limiting pressure is greater in carbon dioxide than in ammonia.

Case in which carbon dioxide is in excess:—

Temperature	Total pressure observed after mixture π	Partial pressure of the gas added in excess P	Difference P−π $=p_1$	Vapour-pressure of the carbamate in a vacuum at temperature considered p	Ratio $\frac{P}{p}$	Ratio $\frac{p_1}{p}$
°	mm.	mm.	mm.	mm.		
20·4	78·9	33·5	45·4	66·2	0·52	0·71
21·8	105·8	69·9	35·9	71·0	0·98	0·81
18·3	112·4	87·4	25·0	55·0	1·59	0·45
18·3	145·4	122·3	23·1	55·0	2·22	0·42
17·9	167·9	148·9	19·0	53·3	2·79	0·36
18·6	203·4	185·5	17·9	56·3	3·28	0·32
17·9	193·3	175·7	17·6	53·3	3·30	0·33
17·8	225·3	208·4	16·9	53·0	3·93	0·32
17·6	243·6	228·5	15·1	52·3	4·37	0·29
18·6	302·9	288·3	14·6	56·5	5·10	0·26
17·7	297·5	285·6	12·9	52·6	5·43	0·24
17·7	328·8	315·8	13·0	52·6	5·99	0·25
18·4	353·7	340·7	13·0	55·5	6·14	0·23
18·4	426·4	416·8	9·6	55·4	7·52	0·18

Case in which ammonia is in excess: –

Temperature	Total pressure observed after mixture π	Partial pressure of the gas added in excess P	Difference P−π $=p_1$	Vapour-pressure of the carbamate in a vacuum at temperature considered p	Ratio $\frac{P}{p}$	Ratio $\frac{p_1}{p}$
°	mm.	mm.	mm.	mm.		
21·8	69·5	24·4	45·1	70·9	0·36	0·67
20·6	75·2	35·4	39·8	65·3	0·54	0·61
20 8	86·9	57·1	29·8	66·2	0·86	0·45
17·7	68·9	48·6	30·3	52·6	0·92	0·39
20·8	88·5	66·1	22·4	66·2	1·00	0·34
22 0	103·5	89·1	14·4	72·1	1·24	0·20
20·8	108·1	93·4	14·7	66·2	1·41	0·22
20·4	111·8	92·6	19·2	64·3	1·44	0·30
17·3	99·7	86·0	13·7	51·2	1·68	0·27
21·7	132·1	125·2	6·9	70·4	1·78	0·10
20·7	154·5	141·6	12·9	65·8	2·15	0·20
17·3	128·0	119·0	9·0	51·2	2·33	0·17
21·7	168·1	165·8	2·3	70·4	2·36	0·03
17·4	155 5	146·4	9·1	51·5	2·84	0·18
21·6	203·3	201·2	2·1	69·9	2·88	0·03
21·7	235·0	232·9	2·1	70·4	3·31	0·03
17·1	180·3	173·3	7·0	50·5	3·43	0·14
20·6	231·1	226·4	4·7	65·3	3·47	0·07
21·8	293·6	292·2	1·6	70·9	4·15	0·02
20·8	295·6	289 2	6·4	66·2	4·43	0·10
21·6	325·9	324·8	1·1	69·9	4·61	0·02
21·9	374·5	372·2	2·3	71·5	5·24	0·03
20·5	417·4	416·2	1·2	64·8	6·42	0·02
17·8	359·8	355·3	4·5	53·0	6·71	0·08

II. *Dissociation in homogeneous systems.*—Theoretically by far the simplest cases; numerical results are, however, obtained with greater difficulty than in the cases last considered.

Amylene bromide (Wurtz, *C. R.* 60, 729). $C_5H_{11}Br$ dissociates when heated into amylene and hydrobromic acid; the dissociation is complete at 360°. Wurtz measured the thermal changes produced by mixing amylene vapour and hydrobromic acid, and found that at 360° the change was zero, and became increasingly positive as the temperature fell (*C. R.* 72). Here then we have for the second time a proof of dissociation; the heat of combination of amylene and hydrobromic acid bears a simple relation to the amount of dissociation as deduced from the vapour density observations. Want of agreement, however, was noticed in some experiments, and attributed by Wurtz to the limit not being obtained in all cases since the velocity is small.

Phosphorus pentachloride PCl_5. Owing to the researches of Wurtz on the vapour density of this body we may consider that, subject to the application of Avogadro's law, dissociation has in this case been demonstrated. The primary object of Wurtz's experiments was to find whether the vapour of phosphorus pentachloride conformed to the law of Avogadro; *assuming* this to be the case, it follows that dissociation must take place in the observed cases of anomalous vapour density. Applying the principle of the action of mass, Wurtz hit on the notion of measuring the vapour density of the pentachloride when it was vapourised into an atmosphere of phosphorus trichloride vapour. From the analogy of other experiments the effect of the trichloride should be to prevent dissociation, supposing it to take place under ordinary circumstances. This was found to be the case, and thus it was proved that phosphorus pentachloride does obey Avogadro's law; or if we assume that Avogadro's law expresses the very nature of the gaseous state under all circumstances whatever, then the dissociation of the pentachloride under ordinary circumstances may be considered to be demonstrated.

The experiments of Cahours were made at ordinary pressures; of Wurtz and of Troost and Hautefeuille at low pressures; the low pressures were produced by Wurtz by the method of mixing air with the vapour, and by Troost and Hautefeuille directly by means of an air-pump. The numbers are:—

Experiments of Cahours at atmospheric pressure.

Temperatures	Vapour Density	Ratio x of PCl_5 combined to PCl_5 possible	Ratio $1-x$ of PCl_5 dissociated to PCl_5 possible
°			
182	5·078	0·58	0·42
190	4·987	0·55	0·45
200	4·851	0·51	0·49
230	4·302	0·32	0·68
250	3·991	0·20	0·80
274	3·840	0·12	0·98
288	2·67	0·03	0·97
289	3·69	0·04	0·96
300	3·654	0·02	0·98
327	3·656	0·02	0·98
336	3·656	0·02	0·98

Experiments of Wurtz.
Low pressures obtained by the diffusion of the vapour into air.

Temperatures	Partial pressure sustained by the diffused vapour	Density of the vapour of the perchloride	Ratio x of PCl_5 combined to PCl_5 possible	Ratio $1-x$ of PCl_5 dissociated to PCl_5 possible
°	mm.			
129	170	6·63	0·91	0·09
129	165	6·31	0·86	0·14
129	191	6·18	0·83	0·17
137	148	6·47	0·88	0·12
137	243	6·46	0·88	0·12
137	234	6·42	0·87	0·13
137	281	6·48	0·89	0·11
137	269	6·54	0·90	0·10
145	311	6·70	0·92	0·08
145	307	6·33	0·86	0·14
145	391	6·55	0·90	0·10

Experiments of Troost and Hautefeuille.
Low pressures obtained directly by a partial vacuum.

Temperatures	Pressure of the vapour	Density of the vapour of the perchloride	Ratio x of PCl_5 combined to PCl_5 possible	Ratio $1-x$ of PCl_5 dissociated to PCl_5 possible
°	mm.			
144·7	247	6·14	0·82	0·18
148·6	244	5·964	0·79	0·21
150·1	225	5·886	0·77	0·23
154·7	221	5·619	0·72	0·29
167·6	221·8	5·415	0·67	0·33
175·8	253·7	5·235	0·62	0·30
178·5	227·2	5·150	0·60	0·40

The results of Troost and Hautefeuille are probably the best, because there is reason to suppose that the limit was not always reached by Wurtz, and he had no right to treat the vapour as accurately fulfilling the law of Boyle.

Lemoine has calculated the influence of an excess of trichloride vapour from the experiments of Wurtz and Cahours.

Hydriodic acid (Lemoine, *C. R.* 1875 and 1877; *A. Ch.* 1877).—Hydriodic acid was chosen by Lemoine as the subject of an exhaustive series of experiments for the following reasons. The chemical constitution of hydriodic acid is the simplest possible for a compound; the products of its dissociation are gaseous at manageable temperatures, and the thermal changes undergone during dissociation are very small; the velocity of the changes is large enough to be manageable.

Velocity of formation or decomposition of hydriodic acid varies enormously with the temperature. At 440° equilibrium is restored almost in an hour; at 350° days are required; while at 260° the period is one of months. The decomposition of hydriodic acid at 260° appears to be much slower than the combination of hydrogen and iodine vapours.

Relation of free to total hydrogen at the end of 8 hours, beginning with (a) hydriodic acid, (b) mixture of hydrogen and iodine.

Temperatures	Hydriodic acid	Mixture of hydrogen and iodine
350°	0·03	0·69
440°	0·22	0·25

Again, the velocity depends on the pressure, being greater the greater the pressure. Thus, at the end of 8 hours—

At a pressure of 4 atmospheres 0·44 free, leaving 0·56 combined.

At a pressure of 2 atmospheres 0·69 free, leaving 0·31 combined.

At a pressure of 1 atmosphere 0·97 free, leaving 0·03 combined.

At the end of 34 hours we shall have—

At a pressure of 4 atmospheres 0·29 free, leaving 0·71 combined.

At a pressure of 2 atmospheres 0·48 free, leaving 0·52 combined.

At a pressure of 1 atmosphere, 0·61 free, leaving 0·39 combined.

The relation of velocity to pressure is rendered clearer by the curves shown in figs. 9, 10, and 11.

The horizontal lines represent the time in days. The vertical lines represent the relation of the free hydrogen to the hydrogen introduced (free hydrogen persisting if we begin with iodine and hydrogen; set at liberty if we start with hydriodic acid).

The value of the limit varies with the temperature and pressure, but varies much less than the velocity. The variation appears to be regular. The effect of pressure is very small but real, and more marked at high temperatures than at low ones. Compression appears to make combination more complete. Special care was taken to insure the attainment of the limit. A small correction has to be made for the action on the glass, this has been determined experimentally and found to make the corrected value of the limit greater than the uncorrected value: a very curious result. The ratio of free to total hydrogen at 4·5 atmospheres is increased about 4 p.c., and at 9 atmospheres about 14 p.c., but these actual values can hardly be considered quite satisfactory. The curve shown in fig. 12 indicates the relation between the limit and the pressure.

Curves representing the proportion of gas remaining free in a mixture of hydrogen and iodine vapour in equal volumes, or in hydriodic acid heated to the temperature of 350° (Lemoine).

Pressure = 4 atmospheres.
Hydrogen and iodine.

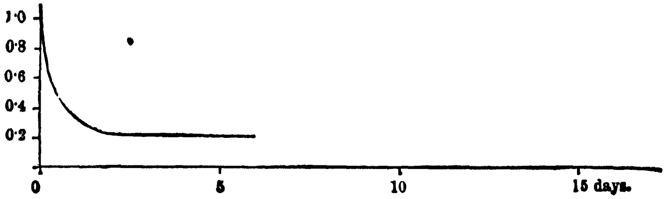


FIG. 9.

Pressure = 2 atmospheres.
Hydrogen and iodine (descending curve).
Hydriodic acid (ascending curve).

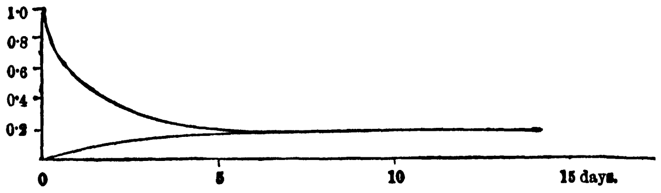


FIG. 10.

The ordinates marked by points represent the relation of the free hydrogen to the total hydrogen calculated when the action of the glass is neglected; the ordinates marked by crosses represent the same relation, taking this action into account, for eight hours' heating.

Excess of one of the elements has the same effect as diminishing the pressure as far as velocity goes, that is, velocity diminishes with an excess of either element.

The influence on the value of the limit is much more marked. 'An excess of either element gives stability to the compound.' This is shown by the curve (fig. 13) and the following table:—

Hydrogen and iodine vapour heated to 440° *in variable proportions, the pressure remaining constant* (Lemoine).

Duration of the experiment in hours	Pressure at 440° of the hydrogen alone atm.	Ratio of the equivalents of iodine and hydrogen	Ratio of free to total hydrogen.
„	2·20	1·000	0·240
5	2·33	0·784	0·350
4	2·33	0·527	0·547
22½	2·31	0·258	0·774
26	0·37	1·360	0·124? (Hautefeuille)
„	0·45	1·000	0·260
8	0·41	0·623	0·676†
14	0·45	0·580	0·614†
9½	0·46	0·561	0·600†
22	0·48	0·526	0·563
22½	0·48	0·256	0·794?

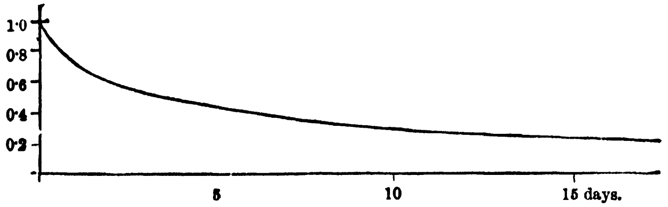
† These three experiments, which lasted respectively 8, 14, and 9½ hours, were not sufficiently prolonged, and the limit was not reached.

In considering the gaseous volumes for a point, *m*, in the curve (fig. 13), *pm* is the volume of hydrogen remaining free, *mr* is the volume of hydrogen combined, and consequently also the volume of iodine vapour combined; the volume of iodine vapour introduced = Ar = *rq* (since AB is inclined at 45 degrees); *mq* is therefore the volume of iodine uncombined. The ratio of the hydriodic acid dissociated to the hydriodic acid possible is therefore that of the lines *mq* and *rq*. If all the iodine combined, the curve would be reduced to the straight line AB. If with an infinitely small quantity of iodine there was no dissociation, the curve would be tangential to AB; this, however, does not occur.

We may take from the curve the ratio of the hydriodic acid dissociated to the 'possible' hydriodic acid, that is to say, the amount of hydriodic acid which would be formed were all the iodine taken up by the hydrogen. In the case where the temperature is 440°, and the partial pressure of the hydrogen is 2·3 atmospheres, we get the following:—

Ratio of the number of equivalents of iodine and hydrogen	Ratio of HI dissociated to HI possible	Ratio of HI persistent to HI possible
1·000H + I	0·24	0·76
1·000H + 0·784I	0·17	0·83
1·000H + 0·527I	0·14	0·86
1·000H + 0·258I	0·12	0·88

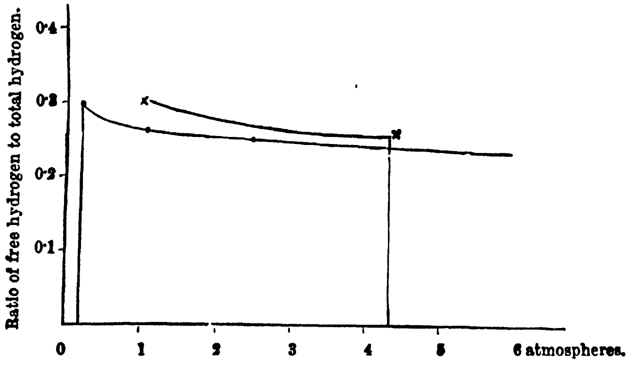
Pressure = 1 atmosphere.
Hydrogen and iodine.



Scales: 0·2 mm. per hour or 4·8 mm. per day: 2 mm. for one-tenth of gas remaining free.

FIG. 11.

Curve representing the relation of the free hydrogen to the total hydrogen, that is to say the limit of decomposition of hydriodic acid, at 440° for different pressures.



Scales: 10 mm. for one atmosphere, and 10 mm. for 0·1 of hydriodic acid decomposed.

FIG. 12.

Again, if we cause 1 equivalent of iodine to act respectively on 1, 2, 3, &c., equivalents of hydrogen, we get the following relations, which may be put in a curve (fig. 14):—

Composition of the system introduced.	Ratio of HI dissociated to HI possible	Ratio of HI persistent to HI possible
H + I	0·26	0·74
2H + I	0·16	0·84
3H + I	0·13?	0·87
4H + I	0·12	0·88

Lemoine considers it probable that an indefinite increase of one of the reacting bodies would never tend to produce total combination of the other. Berthelot doubts this.

Porous bodies, and especially platinum black, alter the velocity enormously, but have only a small influence on the limit. The action of sunlight appears in some cases to destroy the limit entirely, and to cause perfect combination.

Methyl ether and hydrochloric acid (Friedel, *C. R.* 81).—When a mixture of methyl ether and hydrochloric acid is passed through well-cooled tubes a liquid is formed whose composition is variable, and may be considered to be represented by the formula $x(CH_3)_2O + yHCl$. If the gases are merely mixed a dissociable system is obtained, behaving in many ways like the one last considered, but differing from it in that a contraction of volume takes place during the combination of the ether with the hydrochloric acid. This facilitates observation, but makes the application of theory more difficult. The velocity of the reaction is so great as to be unobservable.

The condensation amounts to one-half the volume of the mixed gases.

Vapour density of	oxide of methyl is .	1·592
„ „	hydrochloric acid is .	1·263
„ „	compound if completely formed is .	2·854
„ „	mixture of equal volumes of methyl oxide and HCl is	1·43

I. *Rise of temperature* increases dissociation. Numbers are:—

		Vapour density
If the combination be total		2·884
At the temperature of	5°	1·645
„ „	15°	1·570
„ „	25°	1·537
„ „	35°	1·516
„ „	45°	1·506
„ „	55°	1·498
„ „	65°	1·488
„ „	75°	1·483
„ „	85°	1·474
„ „	95°	1·467
If the decomposition be total		1·430, or 1·442

with the gaseous mixture employed by Friedel.

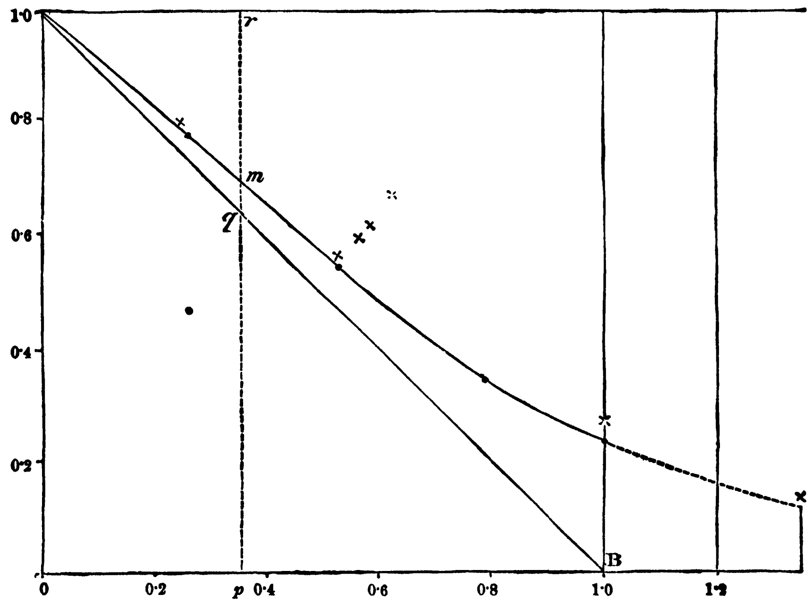
II. *Influence of pressure.*—Dissociation diminishes with increasing pressure, thus:—

		Vapour density
If the decomposition were total		1·430
At the pressure of	670mm. of mercury	1·537
„ „	750 „	1·548
„ „	850 „	1·565
„ „	950 „	1·583
„ „	1050 „	1·602
„ „	1100 „	1·611
If the combination were total		2·854

III. *Influence of an inert gas*, such as air, is the same as that of a reduced pressure.

Curve representing the ratio of free hydrogen to total hydrogen in a mixture of hydrogen and iodine vapour heated to 440° in variable proportions.

The volume of hydrogen OA = OB is constant, and in excess with respect to the iodine.



Numbers of equivalents of iodine for one equivalent of hydrogen.

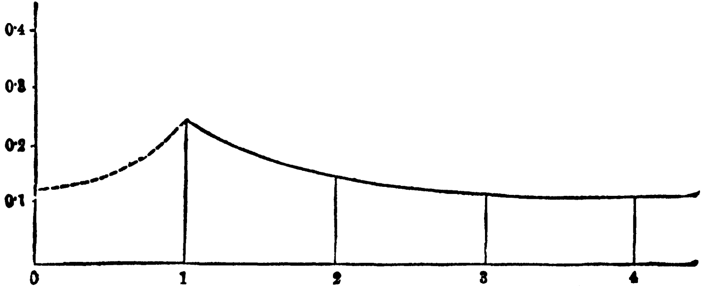
Scales: 7·5 mm. represent 0·1 equivalent of iodine for one equivalent of hydrogen; 7·5 mm. represent 0·1 of hydrogen remaining free for 1·0 of hydrogen introduced.

The curve uniting the points represents the experiments at high pressures.

The crosses represent the experiments at low pressures.

FIG. 13.

Curve representing the ratio of the hydriodic acid dissociated to the hydriodic acid possible in a gaseous system, in which one equivalent of iodine vapour is heated to 440° in presence of variable quantities of hydrogen.



Number of equivalents of hydrogen for one equivalent of iodine.

Scales: 20 mm. for each equivalent of hydrogen: 7·5 mm. for 0·1 of hydriodic acid dissociated.

FIG. 14.

IV. *Effect of excess* is the same as for hydriodic acid. When the temperature is about 20° and the pressure 1 atmosphere, the numbers are the following:—

Excess of oxide of methyl (with respect to the total volume of the mixture)	Contraction (with respect to double the volume of the less abundant gas)
= 0	= 5·8
0·10	7·7
0·20	8·9
0·40	10·8
0·60	11·8

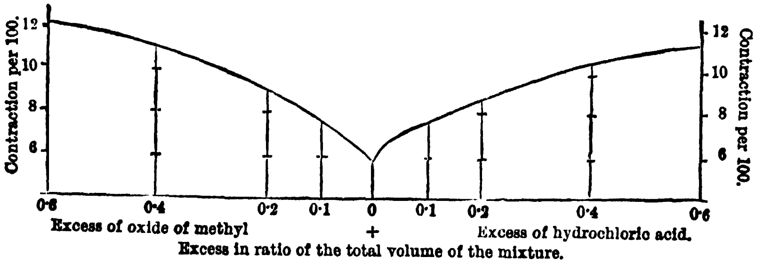
Excess of hydrochloric acid (with respect to the total volume of the mixture)	
= 0	5·8
0·10	7·7
0·20	8·6
0·40	10·4
0·60	11·2

These may be put in a curve thus:—

By a simple calculation the fraction of dissociation may be obtained from the vapour-density observed. If y is the weight of compound dissociated, and p is the total weight per litre, we find that the fraction $\frac{y}{p}$ may be calculated from the equation $\frac{y}{p} = \frac{2\cdot88}{d} - 1$, where d is the observed vapour-density. Thus the influence of temperature is given by the numbers:—

Temperature	ratio $\frac{y}{p}$ dissociated at different temperatures
5°	0·75
15	0·84
25	0·88
35	0·90
45	0·92
55	0·93
65	0·94
75	0·95
85	0·96
95	0·97

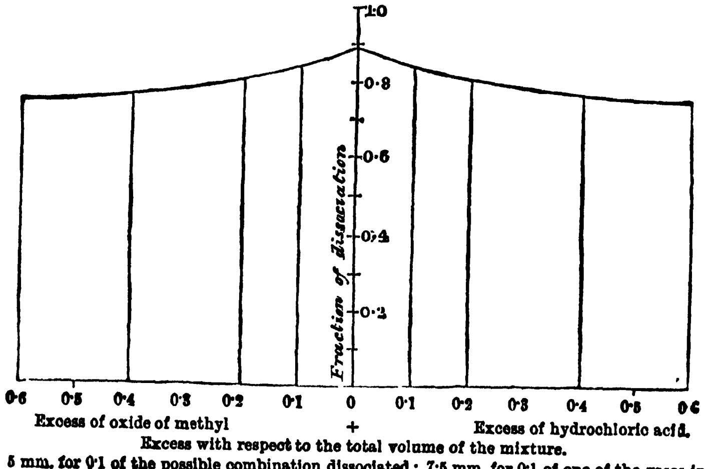
Curve representing the contraction of a mixture of hydrochloric acid and oxide of methyl, in which one of the two gases is in excess.



Scales: 17 mm. for a contraction of 10 per cent. with respect to double the volume of the less abundant gas: 7·5 mm. for 0·1 of one of the gases in excess in a volume of the mixture equal to 1.

FIG. 15.

Curve representing the fraction of dissociation $\frac{y}{p}$ in a mixture of hydrochloric acid and oxide of methyl, when one of the bodies is in excess.



Scales: 5 mm. for 0·1 of the possible combination dissociated; 7·5 mm. for 0·1 of one of the gases in excess in a total volume of the mixture equal to 1.

FIG. 16.

The influence of pressure is given by the numbers:—

Pressure mm.	Ratio $\frac{y}{p}$ dissociated at the same temperature and at different pressures
670	0·88
750	0·86
850	0·84
950	0·82
1,050	0·80
1,100	0·79

When the combination takes place between two gases, of which one is in excess, the reduction is more complicated. However, it is not difficult, and is given by Lemoine, page 89 of his book. The effect of an excess expressed in this way is given by the following numbers, and in the curve, fig. 16:—

Oxide of methyl in excess.

Excess with respect to the total volume of the mixture	Contraction with respect to double the volume of the less abundant gas	Excess μ expressed in equivalents	Fraction of dissociation $\frac{y}{p}$
0	0·058	0	0·884
0·10	0·077	0·222	0·846
0·20	0·089	0·500	0·822
0·40	0·108	1·333	0·784
0·60	0·118	3·000	0·764

Hydrochloric acid in excess.

0	0·058	0	0·884
0·10	0·077	0·222	0·846
0·20	0·086	0·500	0·828
0·40	0·104	1·333	0·792
0·60	0·112	3·000	0·776

The calculations involve an assumption of the applicability of Boyle's law, which is, however, only justifiable in a limited degree, especially with respect to the ether vapour.

Amongst other dissociable systems which have been more or less studied we may notice

Calomel, by Debray (*C. R.* 83, 30).

Ammonium chloride, by Deville (*Leçons*); Pebal (*A. Ch.* [3] 77, 93); Marignac (*Bl.* 1867. vol. 2).

Pebal's researches have been already commented on.

Ammonium sulphide.—Among others, by Bineau (*A. Ch.* 70, 26); Deville and Troost (*C. R.* 56, 891; 88, 1239); Horstmann (*A. Suppl.* 1863); Salet (*C. R.* 86, 1080); Mortessier a. Engel (*C. R.* 1879).

Chloral hydrate.—The subject of much discussion by Troost, Wurtz, Deville, Berthelot, Naumann, &c. Remarkable for an ingenious test introduced by Troost to determine the presence or absence of water-vapour, as well as its pressure, in the vapour of chloral hydrate. The method consists in exposing hydrated salts of known vapour-pressure to the action of the vapour and observing whether they become more or less hydrated. This method, however, appears troublesome in practice, and has hitherto led to contradictory results (*v.* Lemoine, *Études*, 93).

Dissociation of salts in solution *v.* Solution.

Dissociation produced by electrical agency A rough and provisional theory has already been given of the action of the electrical discharge in producing dissociation

Methods employed.

I. A series of sparks may be caused to pass between the terminals of a eudiometer-tube containing the gas to be experimented on. In this case care must be taken to prevent the heating of the terminals, otherwise the rise of temperature produced in their neighbourhood will influence the effects to be observed in an unknown manner.

II. The most powerful arrangement yet devised is the apparatus of Siemens. This consists essentially of two concentric glass tubes; the outer surface of the larger tube and the inner surface of the smaller tube are both coated with some conducting material. The gas to be experimented on passes through the annular space between the two glass tubes. Let the two conducting surfaces be kept at different potentials; then it can be shown that there will be an electrical distribution over the surfaces of discontinuity of the dielectric. That is, there will be a distribution over the inner surface of the outer tube, and over the outer surface of the inner tube. The difference of potential between these two surfaces will increase as the difference of potential between the conducting surfaces increases. A point will finally be reached when the difference of potential of the distribution between the glass surfaces becomes sufficient to produce a breaking down of the insulation of the dielectric, and an ordinary discharge will be the result. The electric field in the instruments generally sold is fairly uniform, and the apparent electric strength of the insulating layer of gas is proportionately large. The discharge, when it does take place, consists of an enormous number of small sparks. It is to this fact that the efficiency of the apparatus is doubtless to be traced.

Ozone.—The subject of many experiments. Hautefeuille and Chappuis (*C. R.* 1880) give the following numbers, for the proportion of ozone formed, as representing the limits at different temperatures and pressures:—

Proportion of ozone by weight.

Pressure	−23°	0°	20°	100°
760 mm.	0·214	0·149	0·106	
380 "	0·204	0·152	0·125	0·0117
300 "	0·201	0·153	0·112	
225 "	0·191	0·153	0·104	0·0118
180 "	0·181	0·137	0·089	

The slow resolution of the mixture of ozone and oxygen produced in any of these experiments into pure oxygen would form a convenient field for experiments on velocity. A certain number of such experiments has been made by Berthelot (*C. R.* 1880):—

	Proportion of ozone
At the commencement	5·3
After 1 day	2·9
2 days	2·1
6 "	1·2
14 "	0·4
51 "	traces
60 "	zero

Nitrogen and Oxygen.— May be caused to combine under the influence of the electric spark. This experiment is chiefly interesting historically.

Nitrogen.—It has already been pointed out that the efficiency of the spark in producing dissociation of an observable character will depend greatly on the form of the discharge. This is a very obscure subject and cannot be treated here. The reader is recommended to consult a paper by J. J. Thomson on the electric discharge in gases (*P. M.* 1883). It is there shown that the pressure must exercise a very important influence on the phenomena to be observed.

At pressures of about 0·8 mm. a discharge of a peculiar kind obtained from an induction coil by inserting a large resistance in the circuit was observed by Thomson and Threlfall (*Pr.* 1886) to produce a contraction in an atmosphere of pure nitrogen. On heating the resulting gas the original volume was recovered. This effect probably points to the production of an allotropic form of nitrogen.

Ammonia forms a dissociable system: the limit is here very high: that is the ammonia may be almost completely decomposed. On the other hand, of course only a very slight combination is produced if we start from nitrogen and hydrogen, though this may be made indefinitely great by removing the ammonia formed. Some peculiar views have been put forward in this connexion by Johnson (*P. B.* 1886, No. 2; *v. also* Pamphlet, *Elementary Nitrogen, and on the Synthesis of Ammonia*, by Johnson [Churchill, 1885]).

Carbon dioxide is decomposable with a very low limit. If a bit of phosphorus be placed in the tube to absorb the oxygen as fast as it is formed the reaction becomes unlimited. The inverse case of carbonic oxide and oxygen is curious. Theoretically, from the experiments on carbon dioxide, combination should take place easily, or rather the limit should be high. However, in an experiment continued for six hours very little carbon dioxide was produced, if any. This may be accounted for if we assume the velocity of the reaction to be extremely slow, though there is no other reason for such an assumption.

Water-vapour, decomposed with difficulty.

Acetylene.—As the products of decomposition are liquid the reaction is unlimited. If the sparks are large, carbon is deposited and the reaction goes on till the gas consists of about seven volumes of hydrogen to one of acetylene. In this case there is an approximate limit. Berthelot has examined its relation to the pressure, and gives the following numbers:—

Pressure in metres of mercury	Limiting proportion of acetylene per 100 volumes
3·46	11·9
0·76	12·0 to 12·5
0·42	11·9
0·41	12·0
0·31	6·5
0·23	3·5
0·18	3·1
0·10	3·1

It will be noticed that the relation is not continuous, this is probably to be traced to the fact that the products of decomposition depend on the kind of spark employed, and this is itself conditioned by the pressure of the gas.

Hydrocyanic acid.—This is formed from acetylene and hydrogen by the action of the spark. The reaction is complicated by the production of other and more complex substances.

Theories of Dissociation.

A. Theories which endeavour to account for the phenomena of dissociation and give results, numerically comparable with experiment, based on the principle of the *action of mass*; Lemoine, Guldberg a. Waage, Van 't Hoff.

B. Theories based on the *kinetic theory of gases*; Clausius and Lemoine.

C. Theories based on the generalisation of the *principles of thermodynamics*; Willard Gibbs, Horstmann, Peslin, Van der Waals.

D. Theory based on the *vortex-atoms hypothesis*; J. J. Thomson.

E. Theory deduced from general equations of dynamics; J. J. Thomson.

THEORY OF THE ACTION OF MASS SIMPLY (Pfaundler and Lemoine).—Let two gases A and B in a system be in circumstances permitting combination. Let there be N molecules of A, and N′ molecules of B, in a certain closed space. Other things being equal, the chance of a molecule of A combining with a molecule of B will be greater the greater the number of molecules of B in its immediate neighbourhood. Similarly the chance of combination of a molecule of B will depend on the number of molecules of A in its immediate neighbourhood. If dy is the amount of combination in time dt we shall have

$$\frac{dy}{dt} = b\,f(\mathrm{N})\phi(\mathrm{N}').$$

If we assume that the functions are identical, which amounts to supposing that an excess of either gas would have the same influence on the result, this becomes

$$\frac{dy}{dt} = b\,f(\mathrm{N})\,f(\mathrm{N}').$$

If the gases do not combine in equal volumes the violent supposition is made that a combination takes place first of all by equal volumes, and that then a further combination goes on with the other volumes step by step. Taking the case of a combination of one volume of A with two of B first of all in time dt we have an amount of compound formed given by the last equation, viz.:—

$$dy = b\,f(\mathrm{N})\,f(\mathrm{N}')\,dt.$$

This then combines with another volume of B or

$$\frac{dy}{dt} = b'f(\mathrm{N}')\,f[b\,f(\mathrm{N})\,f(\mathrm{N}')].$$

A further assumption, that the amount of chemical change is simply proportional to the masses in presence, reduces our first case to

$$\frac{dy}{dt} = b\,\mathrm{NN}'$$

and our second to

$$\frac{dy}{dt} = b\,\mathrm{NN}'^2,$$

where b is a constant.

This, however, except in a few cases, is found to be insufficient to account for experimental results, and Lemoine, therefore, introduces a new constant, thereby abandoning the theory of the action being strictly proportional to the masses in presence, and writes

$$\frac{dy}{dt} = b.\mathrm{N}^{\beta}.\mathrm{N}'^{\beta}$$

and

$$\frac{dy}{dt} = b.\mathrm{N}^{\beta}\,\mathrm{N}'^{2\beta}$$

for the two cases respectively.

The same result may be arrived at from a study of the kinetic theory of gases. Although owing to the assumptions necessary no real knowledge can be gained from the theory in question, still it may be useful to give a summary of it here. The reader will notice the confusion between atoms and molecules.

Let A and A′ be two gases tending to combine in equal volumes, N and N′ the number of 'free molecules' or atoms (?) per unit volume. Let λ and λ' be the mean distances of the two kinds of molecules: then we have

$$\mathrm{N}\lambda^3 = \mathrm{N}'\lambda'^3 = 1.$$

We have to find the chance of combination between the molecules of A and A′. To do this Clausius assumes that two 'molecules' will combine when their centres approach to a distance smaller than $2l$ where l is called the 'radius of chemical activity' of each molecule. The molecules of both gases are supposed to be in motion in accordance with the well-known laws of the kinetic theory, the whole of which as far as principles go is here assumed. Instead of explicitly considering the velocities of both systems, Clausius shows that matters are simplified if we consider the molecules of A at rest, and the molecules of A′ endowed with a velocity of

$$u = v + \tfrac{1}{3}\frac{v'^2}{v^2} \text{ if } v' < v, \text{ and } u = v' + \tfrac{1}{3}\frac{v^2}{v'^2} \text{ if } v' > v;$$

v and v' being the velocities of mean square of the two systems. The probability of a molecule of A′ 'penetrating the sphere of action' of a molecule of A during its passage between two planes perpendicular to one another, and at a small distance S apart, is found by Clausius to be $\frac{\pi l^2}{\lambda^3}\mathrm{S}$. During a time dt, however, a molecule of A′ will go over a space udt with respect to the molecules of A supposed to be at rest. The chance of combination during this time is therefore $\frac{\pi l^2}{\lambda^3}udt$; or substituting for λ^3, $\pi l^2 udt\mathrm{NN}'$. Therefore, the number of molecules $-d\mathrm{N} = -d\mathrm{N}'$ combined in time dt is $-\mathrm{NN}'\pi l^2 udt$.

Let dy be the number of molecules of the compound formed in time dt, then we have

$$\frac{dy}{dt} = \pi l^2 u\mathrm{NN}'$$

or collecting constants, remembering that 'u' is a function of the temperature only,

$$\frac{dy}{dt} = k\mathrm{NN}'$$

which we got before. But we know that this formula is only approximate, and therefore we may as well admit at once that the theory is insufficient. At best, however, the idea of a 'radius of chemical affinity' is only a diagrammatic way of regarding the process of combination. If we consider the action of temperature and pressure the case is still worse, for in default of any information at all we are obliged to regard the radius of chemical activity as remaining constant when the temperature changes. This, of course, again leads to incorrect results, and, therefore, l is supposed to vary in a manner to satisfy the experiments, leaving us exactly where we were before. Again, taking Lemoine's form of expression involving the constant β, we find that to account for the behaviour of hydriodic acid the 'constant' has to be made to vary; thus, at a temperature of 350° it has a value assigned to it of ·8, and at 440° it is reduced to ·553 or ·6 as seems most convenient. Other people (Guldberg a. Waage for instance) avoid the difficulty by putting several constants in to begin with. We may also note the following hints which are given us by the kinetic theory of gases, and which do not involve any special theory of the mechanism of chemical combination. Change of combination-phenomena with change of pressure ought to be slow, since the mean distances of the molecules vary inversely as the cube root of the pressure. Since the kinetic theory gives a tolerably reasonable account of the mechanical meaning of rise of temperature, any information as to what chemical combination really is will most likely be drawn from a study of the dependence of chemical action on the temperature.

The action of pressure and temperature has been investigated by Clausius, but here again special assumptions are made.

GULDBERG AND WAAGE'S THEORY OF DISSOCIATION is sufficiently indicated in the articles AFFINITY and CHEMICAL CHANGE (vol. i.; *v.* especially pp. 70, 73, 737, 746; *v. also* EQUILIBRIUM, CHEMICAL).

THEORIES BASED ON THERMODYNAMIC CONSIDERATIONS.—Certain very important ideas appear to have been put forward by Clausius in his discussion of the term 'Disgregation.' We shall have to consider them when we come to the formal theory of Horstmann. At present it will be more convenient to take a very simple case, which seems first to have been deduced at some length from Clausius' results by Peslin (*A. Ch.* 1871).

Peslin considers the case of carbonate of lime and its decomposition by heat. According to Debray the changes which take place are perfectly reversible, and Peslin applies the general equation of Clausius for reversible systems to this particular case. For information of this general kind *v.* Clausius' *Mechanical Theory of Heat* (translated by W. R. Brown), and Maxwell's *Theory of Heat*.

Assuming the reversibility of the reaction in question (on which point *v. supra*), we may consider a reversible engine driven by the passage of heat from a mixture of carbonic acid, carbonate of lime, and lime, in a hot vessel, to the same mixture contained in a vessel at a lower temperature.

Let T be the absolute temperature of the hot vessel.

Let $T-\epsilon$ be the absolute temperature of the cold vessel.

Let u be the volume occupied by unit weight of calcium carbonate before dissociation; u' the volume occupied by the same weight after dissociation.

Let L be the 'latent heat' of dissociation, which in this case is positive; p is the maximum pressure of dissociation at the high temperature; J is the mechanical equivalent of heat.

Then $u'-u$ is the volume developed by the motion of the piston of the machine during the dissociation of unit weight of substance, and $\frac{dp}{dt}\epsilon$ is the difference of pressure on opposite sides of the piston.

The work done, therefore, during this passage is

$$(u'-u)\frac{dp}{dt}\epsilon.$$

By Carnot's principle the heat transformed into work is

$$L\left\{\frac{T-(T-\epsilon)}{T}\right\}=\frac{\epsilon}{T}L;$$

therefore the equation of heat transformation is

$$(u'-u)\frac{dp}{dt}\epsilon=J.L.\frac{\epsilon}{T}$$

$$\text{whence}\quad L=\frac{T}{J}(u'-u)\frac{dp}{dt}.$$

Now

$$u'-u=\left(1-\frac{u}{u'}\right)u'=\left(1-\frac{u}{u'}\right)\frac{1+at}{\delta_0}.\ \frac{p_0}{p}\ \text{approx.}$$

where a is the coefficient of expansion, and this will be nearly that of a perfect gas, and δ_0 is the density of the carbonic acid of dissociation reduced to 0° and pressure p_0. Substituting this value for $u'-u$ and rearranging, we have

$$\frac{dp}{p}=\frac{J}{p_0}\left[\frac{L\delta_0}{\left(1-\frac{u}{u'}\right)}\right]\left\{\frac{adt}{(1+at)^2}\right\}.$$

Now $\frac{J}{p_0}$ is constant: $\frac{L\delta_0}{1-\frac{u}{u'}}$ is nearly so, sufficiently nearly for our present purpose where we do not intend to deal with any very great range of temperature. In fact between 1040° and 860° the expression does not change in value more than ·2 per cent.

If the engine works from a pressure P_2 to a pressure P_1 we have

$$\int_{P_1}^{P_2}\frac{dp}{p}=\frac{J}{p_0}\left\{\frac{L\delta_0}{\left(1-\frac{u}{u'}\right)}\right\}^2\int_{T_1}^{T_2}\frac{a\delta t}{(1+at)^2}$$

where T_2 and T_1 correspond to P_2 and P_1 respectively.

Solving this equation

$$\log_\epsilon\frac{P_2}{P_1}=\frac{J}{p_0}\left[\frac{L\delta_0}{1-\frac{u}{u'}}\right]^2\left(\frac{1}{1+aT_1}-\frac{1}{1+aT_2}\right).$$

Now we may get all these values from experiment, and therefore choose one to calculate, say L; and then compare with experiment. Peslin, however, uses a rougher method by considering the engine worked with steam, and taking the expression $1-\frac{u}{u'}$ as the same for both water and steam on the one hand, and carbonate of lime and the products of its decomposition on the other. Regnault's value for L for water at 69·1° is 558·2 cal., and the comparison will be made at such temperatures that 69·1 is the mean of $T_1=48{\cdot}4$, and $T_2=89{\cdot}8$, corresponding to the vapour pressures $P'_1=85$ mm. and $P'_2=520$ mm. This gives for the latent heat of dissociation of carbonic acid, if Δ_0 is the density of steam corresponding to δ_0,

$$L=558{\cdot}2\frac{\Delta_0}{\delta_0}\left\{\frac{\frac{1}{1+at_1}-\frac{1}{1+at_2}}{\frac{1}{1+aT_1}-\frac{1}{1+aT_2}}\right\}.$$

Putting in values, $L=666{\cdot}7$; finally comparing this with the value deduced from Favre and Silbermann's results, we find that it is 5 p.c. smaller than it ought to be. Considering the assumptions made as to the applicability of Boyle's law, &c., this is at least as good as one can expect, and may be taken as some evidence that the dissociation process in question is really a reversible operation. This example has been dwelt on at more length than it intrinsically deserves, because it affords a very instructive example of the methods pursued in theories based on thermodynamic considerations. We pass on to

Horstmann's theory (*A.* 170).—Clausius has thrown Thomson's views on the degradation of energy into the following form: 'The entropy of a system will always tend towards a maximum defined by the other conditions to which the system is exposed.'

There is no reason why this should not apply to systems undergoing dissociation. During dissociation some of the changes tend to increase, and some to diminish, the entropy of the system; according to the theory, equilibrium will be attained when the entropy has arrived at its maximum value, *i.e.* when its variation vanishes. Clausius has introduced the term 'disgregation of a system,' and defines it as a quantity depending on the arrangement of the parts of a system, in so far as it is the value of the entropy for the state of the system which it thus defines.

'Let x be the proportion of a body expressed in molecular weights which decomposes or combines with another.' This quantity x may then be regarded as a measure of the degree of dissociation. All the other quantities which vary during dissociation may then be regarded as functions of x. Horstmann's condition of equilibrium is thus $\frac{ds}{dx}=0$ where s is the entropy. Let Q be the quantity of heat which is concerned in the dissociation of an amount of the body equal to the formula weight expressed in grams; then Q, for instance in the case of hydrochloric acid, would be the heat required to dissociate 36·5 grams. To produce the reaction in question we should require Qx units of heat. If T is the absolute temperature, and Z the disgregation of the system, we have

$$s = \frac{Qx}{T} + Z$$

and the condition of equilibrium is found by differentiation of

$$\frac{ds}{dx} = \frac{1}{T}\left(Q + \frac{dQ}{x dx}\right) + \frac{dz}{dx} = 0.$$

As an example, we may apply this equation to the special case of a body decomposing into two others. Let there be one equivalent at the beginning of the process, and suppose there remains undecomposed at the instant considered a quantity x, then the result is to give r molecules of one and s of the other, and let m be the weight of one of the substances in excess; then the three bodies in presence are:—

$$x$$
$$r(1-x)+m$$
$$s(1-x).$$

If Z_1, Z_2, Z_3 are the disgregations corresponding to one equivalent of each of the three states, we have

$$Z = xZ_1 + [r(1-x)+m]Z_2 + s(1-x)Z_3.$$

Suppose further that the system is one like carbonate of lime where one of the products is solid and one gaseous; then Z_1 and Z_2 are independent of x, and Z_3 depends only on the volume available. If u is the volume of one equivalent of the gas generated, Clausius gives

$$Z_3 = Z'_3 + AR\log\frac{u}{u_0}$$

where Z'_3 is the disgregation corresponding to the same mass of gas reduced to standard conditions, *i.e.* to a volume u_0. R is the well-known constant used by Clausius to express the gaseous laws, *i.e.* $\frac{p_0 r_0}{a}$ where $a = 273$; and A is Joule's equivalent. If p is the pressure of the gas we have

$$up = RT.$$

Q in this case consists of two parts, of the heat taken up in producing the chemical change, and $Q-q$ required to do external work, in this case to the extent Apu or ART.

The equation of equilibrium therefore reduces to

$$\frac{q}{T} - AR\log\frac{u}{u_0} + C = 0,$$

where $C = Z_1 - rZ_2 - sZ_3$, the change of disgregation which would take place if the gas had the volume u_0; this therefore is independent of x; u only varies as the action proceeds, and the equation therefore expresses the fact that the pressure must be determinate for the condition of equilibrium.

The method has been applied by Horstmann to calculate the pressures produced by the dissociation of amylene bromide and phosphorus pentachloride.

Phosphorus pentachloride.—The agreement is fairly satisfactory, as may be seen by the following curves (fig. 17) which are given by the theory; the points correspond to observations, two of which are used to calculate each curve.

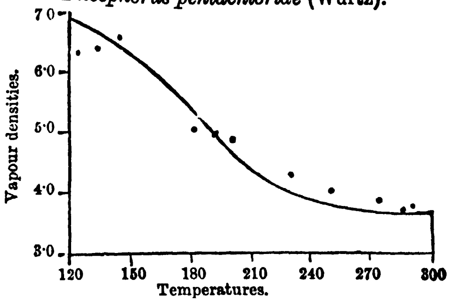
Lemoine has calculated the values of x by an appropriate modification of the above equation for hydriodic acid, and finds that the agreement is within 5 p.c.

It may be noticed about this theory that if the quantity of heat absorbed or given out during the reaction was zero, the limit would be independent of the temperature; this actually occurs very nearly in cases of etherification, and the conclusion coincides with experimental results.

A difficulty is that dissociation, according to the theory, would go on to absolute zero, while as a matter of fact it is generally supposed only to begin at a certain point. As to this it may be said that below a certain point the dissociation has hitherto avoided detection.

The influence of an excess of one constituent is extremely well and concordantly brought out by the theory. The influence of the pressure will be zero as far as the limit is concerned if no condensation or expansion occurs; as for instance in the dissociation of hydriodic acid.

Phosphorus pentachloride (Wurtz).



Amylene bromide (Cahours).

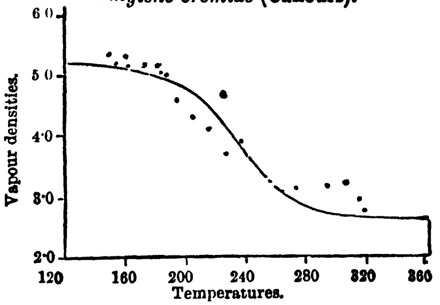


FIG. 17.

No information is given by the theory as to the progress of the reaction, *i.e.* we get no information from it as to velocity.

THEORY OF GIBBS (*Am. S.* 18).—This theory has many points of resemblance with that of Horstmann, as will be seen by the following statement of the principles:—

1. For the equilibrium of an isolated system it is necessary and sufficient that in all the possible variations of the state of the system, the energy being maintained constant, the variation of the entropy shall be zero or negative.

2. Similarly, if the entropy be constant the variation of energy must be zero or positive if equilibrium is to be preserved.

Applying these principles to a mixture of gases obeying Boyle's law, &c., we have for the energy of the mixture

$$M_1(C_1t+E_1) + M_2(C_2t+E_2) + \ldots\ldots\ldots\ldots$$

M_1 and M_2 are the masses of the different gases. C_1 and C_2 are the sp. heats at constant volume. E_1 and E_2 are other constants, and t is the absolute temperature.

Similarly the entropy is given by

$$M_1(H_1 + C_1\log_e t - a_1\log\frac{M_1}{V}\Big)$$

$$+ M_2(H_2 + C_2\log_e t - a_2\log\frac{M_2}{V}\Big) + \dots\dots\dots\&c.$$

Where V is the volume, H_1, A_1, H_2, A_2 are constants depending on the nature of the gas such that a_1 and a_2 are inversely proportional to the densities.

Gibbs assumes that these equations will also apply to a system of gases in which chemical change takes place. If we consider a system in which the energy does not vary, and in which the entropy has its maximum value, then we have one case where equilibrium is established according to the principles laid down. The condition for maximum entropy comes to be the condition that no variation of entropy shall occur when the energy and volume are constants; these two conditions together will give the following:—

$$(H_1 - a_1 - C_1 - \frac{E_1}{t} + C_1\log t - a_1\log\frac{M_1}{V})dm_1$$

$$+ (H_2 - a_2 - C_2 - \frac{E_2}{t} + C_2\log t - a_2\log\frac{M_2}{V})dm_2$$

$$+ \dots\dots\dots\dots\dots\dots\dots\dots\&c. = 0.$$

This equation leads to the result that when the gaseous compound is capable of being formed without condensation, the limit of dissociation will be independent of the pressure. In other cases the dissociation will be a function both of temperature and pressure. Comparisons with experiment in the two cases (hydriodic acid and methyl ether and hydrochloric acid) show that the experimental and calculated results agree very well. A comparison with nitrogen tetroxide, formic acid, acetic acid, and phosphorus chloride vapour, has been made by Gibbs; as an example of the agreement of theory and experiment, we give the following table referring to phosphorus pentachloride:—

Temperature	Pressure	Density		Authors of the experiments
		Calculated	Observed	
°	mm.			
336	760	3·610	3·656	Cahours
327	754	3·614	3·656	„
300	765	3·637	3·654	„
289	760?	3·656	3·69	„
288	763	3·659	3·67	„
274	755	3·701	3·84	„
250	751	3·862	3·991	„
230	746	4·159	4·302	„
222	753	4·344	4·85	Mitscherlich
208	760?	4·752	4·73	Cahours
200	758	5·018	4·851	„
190	758	5·368	4·987	„
178·5	227·2	5·053	5·150	Troost a. Hautefeuille
175·8	253·7	5·223	5·235	„
167·6	221·8	5·456	5·415	„
154·7	221	5·926	5·619	„
150·1	225	6·086	5·886	„
148·6	244	6·199	5·964	„
145	391	6·45	6·55	Wurtz
145	311	6·37	6·70	„
145	307	6·36	6·33	„
144·7	247	6·287	6·14	Troost a. Hautefeuille
137	281	6·53	6·48	Wurtz
137	209	6·51	6·54	„
137	243	6·48	6·46	„
137	234	6·47	6·42	„
137	148	6·31	6·47	„
129	191	6·59	6·18	„
129	170	6·56	6·63	„
129	165	6·55	6·31	„

E. and L. Natanson have discussed the theory in their paper on nitrogen tetroxide (*W. A.* April 1886).

If the thermal changes accompanying dissociation are small, then the theory indicates that the change of dissociation with temperature will be slow. No account is taken either in this theory or in the theory of Horstmann of the supposed thermal change requisite before dissociation begins: both theories would point to the occurrence of dissociation down to absolute zero.

Again these theories are not in any sense molecular. Entropy is a quantity referring to the changes of heat into work and *vice versâ*, and a molecular theory to be satisfactory must obliterate the distinction between heat and kinetic or potential energy.

Theory of J. J. Thomson (*P. M.* [5] 15, 427; 17, 233).—In this theory the views of Clausius a. Williamson as to chemical combination are expressed in terms of the vortex-ring theory of matter. The principles and methods adopted, however, are applicable to any theory of matter, provided only that it involves the principle of discontinuity. The advantages of this theory are that, while it is as general in its application as the theories of Horstmann and Gibbs, it affords a definitely mechanical view of the mechanism by which an equilibrium may be brought about. As has been pointed out several times, any theory based on the kinetic theory of gases is open to the same objection as that theory itself, viz. that even supposing it were brought into harmony with every conceivable experiment, we should really be no further advanced in real knowledge than we are at present, since the assumptions on which it is based themselves require explanation. The vortex-ring theory, however, does not involve such assumption; its premises are merely those of dynamics, and anything we get from it is a real gain since it cannot be twisted about to save appearances.

The account of the theory as given by Thomson is so exceedingly terse that it cannot well be abstracted, and we therefore refer the student to the original papers.

In the article Equilibrium, chemical, will be found a treatment of dissociation-processes as special cases of chemical equilibrium.

R. T.

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18. Ditte, *C. R.* 1872 (Hydrogen selenide).
19. Dixon, *T.* 1884 (Chemical change in gases).
20. Duhem, *J. de Ph.* 1886 (Application of Gibbs' theory).
21. Dumas, *A. Ch.* 1834 (Chloral hydrate).
22. Engel (with Moitessier), *C. R.* 1879 (Ammonium sulphide); *C. R.* 1878–1879, 1880 (Chloral hydrate).
23. Favre, *C. R.* 1868, 1876, 1878 (Influence of porous bodies);
with Valson, *C. R.* 1872 (Chrome alum).
24. Frankland, *T.* 1861, *C. R.* 1868 (Luminosity of flames).
25. Fremy, *v.* Becquerel.
26. Friedel, *Bl.* 1875 (Oxide of methyl and hydrochloric acid).
27. Gay-Lussac, *A. Ch.* 63 (Carbonate of lime).
28. Gautier, *C. R.* 1876 (Alkaline bicarbonates).
29. Gernez, *C. R.* 1867 (Alkaline bicarbonates).
30. Gibbs, *Am. S.* 1879 (Theory).
31. Gladstone (with Tribe), *Pr.* 19, *C. J.* 5 (Velocity of reactions, &c.).
32. Grove, *T.* 1847.
33. Guldberg a. Waage, *Études sur les affinités chimiques* (published by Brogger and Christie, Christiania, 1867); *J. pr.* 1879 (Theory).
34. Harcourt a. Esson, *T.* 1866 (Theory, &c.).
35. Hautefeuille a. Chappuis, *C. R.* 1880 (Ozone). For other papers *v.* Troost.
36. Hittorf, *P.* 126 (Phosphorus).
37. Horstmann, *A.* 155, *Bl.* 1870, 1878 (Acetic acid); *A.* 1877 (Ammonia and carbonic acid. Theory); *A.* 1863 (supplement), *Bl.* 1869 (Ammonium sulphide); *A.* 1873, 1877 (Theory).
38. Isambert, *C. R.* 1878 (Dissociation of chlorine compounds, &c.).
39. Joulin, *A. Ch.* 1873 (Carbonates of silver and manganese); *A. Ch.* 1881, *C. R.* 1880 (Porous bodies).
40. Lecoq de Boisbaudran, *C. R.* 1874, 1875 (Chrome alum).
41. Lemoine, *Études sur les équilibres chimiques*, 1881 (published by Dunod, 49 Quai des Augustins); *A. Ch.* 1871 (Phosphorus. Theory); *C. R.* 1875 a. 1877, *A. Ch.* 1877 (Hydriodic acid); *A. Ch.* 1872 (Theory).
42. Lieben, *Bl.* 1865 (Vapour densities); *C. R.* 1879 (Iodine vapour).
43. Lockyer, *C. R.* 1873, *N.* 1870 *et seq.* (Dissociation).
44. Mahn, *v.* Birnbaum.
45. Marignac, *Bl.* 1867 (Ammonium chloride).
46. Mascart, *Revue scientifique*, 1873 (Vapour densities).
47. Meier, *v.* Crafts.
48. Meyer (Victor), *B.* 1879 a. 1880 (Vapour densities).
49. Myers, *C. R.* 1873 (Oxide of mercury); *A.* 1871 (Hydrogen sulphide).
50. Michaelis, *A.* 170 (Sulphur chlorides).
51. Mitscherlich, *P.* 1833 (Nitrogen tetroxide).
52. Moitessier (a. Engel), *C. R.* 1878, 1879, 1880 (Ammonium sulphide and chloral hydrate).
53. Montier, *A. Ch.* 1874, *C. R.* 1871, 1873, 1874 (Theory).
54. Muller, *A.* 1862 (Nitrogen tetroxide).
55. Muir a. Wilson, *Elements of Thermal Chemistry.*
56. Natanson (E. a. L.), *W.* 1886 (Nitrogen tetroxide, and discussion of theory).
57. Naumann, *Grundriss der Thermochemie*, 1869, *B.* 1874 (Hydrated cupric sulphate); *B.* 1878 (Nitrogen tetroxide); *A.* 1871 (Ammonia and carbonic acid); *B.* 1876, 1879 (Chloral hydrate).
58. Ostwald, *J. pr.* 16 (Theory). Also *Lehrbuch der Allgemeinen Chemie.*
59. Pebal, *A. Ch.* [3] 67 (Ammonium chloride).
60. Peslin, *A. Ch.* 1871 (Theory).
61. Pfaundler, *P.* 182 (*Jubelband*), 131, *B.* 1876 (Theory).
62. Playfair a. Wanklyn, *Pr. E.* 4 (Nitrogen tetroxide and acetic acid).
62a. Ramsay a. Young, *T.* 1886, 1887; *P. M.* 1887; *C. J.* 1886.
63. Raoult, *C. R.* 1881 (Carbonate of lime).
64. Robinson, *v.* Wanklyn.
65. Rose, *P.* 1839 (Ammonia and carbonic acid).
66. Salet, *C. R.* 1868 (Nitrogen tetroxide).
67. Schloessing, *C. R.* 1872 (Bicarbonates of calcium and barium).
68. Thénard, *C. R.* 1872 (Discharge in gases).
69. Thomsen, *P.* 1869, *B.* 1877 (Acids and bases).
70. Thomson, J. J., *P. M.* [5] 15, 17 (Chemical combination in gases);
a. Threlfall, *Pr.* 1886 (Nitrogen).
71. Tribe, *v.* Gladstone.
72. Troost a. Hautefeuille, *Ann. scientifiques de l'école normale*, 1873, *A. Ch.* 1874,

C. R. 1878 (Phosphorus); *Ann. de l'école supérieure*, 1873, *C. R.* 1868 (Cyanogen and cyanic acid); *C. R.* 1874, *A. Ch.* 1874 (Metallic hydrides); *C. R.* 1871 a. 1877 (Formation of compounds at high temperatures); *C. R.* 1876 (Phosphorus pentachloride).

TROOST, *C. R.* 1878 (Acetic acid); *C. R.* 1880 (Iodine); *C.R.* 1877-1879 (Chloral hydrate); *A. Ch.* 1878 a. 1881 (Chloral hydrate).

73. URBAIN, *C. R.* 1876 (Alkaline bicarbonates).

74. VAN DER WAALS, *On the Continuity of the Liquid and Gaseous States.*

75. VAN 'T HOFF, *B.* 1877 (Theory).

76. VIEILLE, *C. R.* 1882, 1883 *et seq.* (Explosive pressures and dissociation).

77. VICAIRE, *C. R.* 1868, *A. Ch.* 1870 (Theory).

78. WAAGE, *v.* GULDBERG.

79. WANKLYN (with PLAYFAIR, *v.* PLAYFAIR); with ROBINSON, *C. R.* 56 (Sulphuric acid vapour and phosphorus pentachloride).

80. WEINHOLD, *P.* 149, *J.* 1879 (Carbonate of lime).

81. WIEDEMANN, *C. R.* 1878 (Dissociation of salts); *P.* 1874 (*Jubelband*), *J. pr.* [2] 9, (Hydrated salts); with SCHULZE, *W.* 6 (Chloral hydrate).

82. WILLIAMSON, *C. J.* 4, *P. M.* [3] 37 (Chemical theory).

83. WURTZ, *C. R.* 1865 a. 1877 (Amylene bromide); *C. R.* 76, *Bl.* 1873 (Phosphorus pentachloride); *Leçons Société chimique*, 1863, *French Association*, 1873 (Ammonium chloride); *C. R.* 1877-1879 (Chloral hydrate).

DISTILLATION. The conversion of a substance into vapour, and the condensation of the vapour into a liquid by cooling in another part of the apparatus, is called *distillation.* If the vapour is condensed to a solid the process is called *sublimation.* The object of conducting a distillation is usually to separate one body from another which vapourises at a higher temperature than the first. The name *fractional distillation* is often given to the process of separating two or more liquids by taking advantage of differences in their boiling points. When a solid body is decomposed by heat, and the products, or some of them, are condensed to the liquid form and collected, the process is called *dry*, or *destructive*, *distillation*; for instance, when coal is strongly heated in a closed vessel, ammonia, various gaseous hydrocarbons, many liquid and solid hydrocarbons, phenol, and many other compounds, are produced.

The essential parts of all apparatus for distillation are (1) a vessel in which the substance is heated, (2) a means for cooling the products formed by heat, and (3) a receiver to retain the condensed product or products. The ordinary form of distillation-apparatus is a flask connected with a tube, which passes inside a wider tube through which a stream of cold water circulates; a small flask or other suitable vessel is used as a receiver. Various devices are employed in fractional distillation to insure as complete a separation as possible of the more volatile from the less volatile portion of the liquid distilled.

References.—The history of distillation is fully treated in Kopp's *Beiträge der Geschichte der Chemie*, Stück i. 217 *et seq.*; *v.* also E. Wiedemann, *Zeitschr. der deutschen Morgenländischen Gesellschaft*, 32, 575. Various forms of apparatus for fractional distillation are described by Konowalow, *B.* 17, 1531; Wurtz, *A.* 93, 108; Glinsky, *A.* 175, 381; Linnemann, *A. Ch.* [3] 42, 131; Le Bel a. Henninger, *B.* 7, 1084; Hempel, *Fr.* 20, 502; Kreis, *A.* 224, 259. Papers on the theory of fractional distillation, with experimental results, will be found in *C. J.* 35, 544 (Thorpe), and 547 (Brown).

M. M. P. M.

DITA BARK. Dita, the bark of *Echites scholaris*, a tree growing in the Philippine Islands, contains ditaine, accompanied by two other alkaloids, ditamine and echitenine, and by several indifferent substances echicaoutchin, echicerin, echitin, echitein, and echiretin (Gorup-Besanez, *A.* 176, 88; Jobst a. Hesse, *A.* 176, 326; 178, 49; 203, 144; 11, 1546; *B.* 13, 1841; Harnack a. Merck, *B.* 11, 2004; 13, 1648). It is used as a febrifuge.

Ditaïne $C_{22}H_{28}N_2O_4$. *Echitamine.* [206°]. $[\alpha]_D = -28{\cdot}8°$ in a 2 p.c. solution in 97 p.c. alcohol.

Preparation.—Dita bark is boiled with hot alcohol, the extract evaporated, and the residue treated with dilute NH_3 and shaken out with ether. The ether dissolves ditamine; the residue is treated with solid KOH and extracted with $CHCl_3$. The extract is evaporated and treated with conc. HClAq; ditaïne hydrochloride separates while echitenine remains in solution.

Properties. — Vitreous prisms (containing 4 aq). M. sol. water, $CHCl_3$, and ether, v. sol. alcohol, v. sl. sol. benzene, insol. ligroin. Strongly alkaline, except after removal of all water of crystallisation. Conc. H_2SO_4 dissolves it with purple-red colour; HNO_3 gives a purple-red becoming green. Decomposes NaCl, setting NaOH free. Not ppd. from its salts by NH_3. After boiling with dilute HCl its solution reduces Fehling's solution. On evaporating an aqueous solution of ditaine atmospheric oxidation takes place with formation of 'oxyditaine.'

Salts.—B'HCl: crystalline, sol. water, sl. sol. HClAq and solutions of metallic chlorides. $[\alpha]_D = -57°$.—$B'_2H_2PtCl_6$ 3aq: yellow flocculent pp.—B'HBr: prisms.—B'HI.—$B'H_2CO_3$ $1\frac{1}{2}$aq: prisms or crystalline powder.—Sulphate: needles.—Picrate: golden flocculent pp.—Tannate: white flocculent pp.—$B'_2H_2C_2O_4$: powder, sl. sol. alcohol, v. e. sol. water.

Ditamine $C_{16}H_{19}NO_2$. [75°]. Occurs in dita bark to the extent of ·04 p.c. Obtained as above. Ammonia ppts. it from its solution in dilute acids as amorphous flocculæ. V. sol. alcohol, ether, benzene, and $CHCl_3$.—$B'_2H_2PtCl_6$: pale golden flocculent pp.

Echitenine $C_{20}H_{27}NO_4$. [above 120°]. Extracted from dita bark as above; the solution of its hydrochloride is ppd. by $HgCl_2$, the pp. decomposed by H_2S, KOH added, and the base extracted with chloroform. Brownish, very bitter powder. V. sol. alcohol, sl. sol. water chloroform, and ether, v. sl. sol. ligroïn. Alkaline to litmus. Its solutions in conc. H_2SO_4 and HNO_3 are violet. Its salts are amorphous.—$B'_2H_2PtCl_6$: golden flocculent pp—

$B'H_2HgCl_4 2aq$: yellow amorphous powder. Yields trimethylamine when heated with alkalis.

Echicaoutchin $C_{25}H_{40}O_2$. A yellow resinous body, present, according to Hesse, among the products that may be extracted by ligroïn from dita bark, and freed from echicerin by boiling alcohol.

Echicerin $C_{30}H_{48}O_2$. [157°]. $[\alpha]_D = 64°$ (in ether). Occurs in dita bark. Needles (from alcohol); v. sl. sol. cold alcohol, v. sol. ether, ligroïn, acetic ether, and $CHCl_3$, insol. water, alkalis, and acids. Bromine converts it into bromo-echicerin $C_{30}H_{47}BrO_2$, a white powder [116°]. By treating a solution of echicerin in ligroïn for two months with sodium amorphous echiceric acid $C_{30}H_{46}O_4$ is said to be formed.

Echitin $C_{32}H_{52}O_2$. [170°]. S. ·07 in 80 p.c. alcohol at 15°; $[\alpha]_D = 75°$ (in $CHCl_3$). Accompanies echicerin, from which it differs in being less soluble in ligroin. Br gives crystalline $C_{32}H_{51}BrO_2$ [100°].

Echiteïn $C_{42}H_{70}O_2$. [195°]. S. ·1 in 80 p.c. alcohol. $[\alpha]_D = 85°$ (in $CHCl_3$). Occurs in the mother-liquor from which the mixture of echicerin and echitin has separated. Light prismatic needles (from alcohol). Bromine gives $C_{42}H_{67}Br_3O_2$ [150°].

Echiretin $C_{35}H_{56}O_2$. [52°]. $[\alpha]_D = 55°$ in a 2 p.c. ethereal solution. Occurs in the mother-liquor from which echiteïn has crystallised. Translucent mass, v. sol. ether, ligroin, and boiling alcohol.

DITHIONATES, salts of dithionic acid $H_2S_2O_6$; *v.* under SULPHUR, OXYACIDS OF.

n-**DODECANE** $C_{12}H_{26}$. [−12°]. (90°) at 10 mm.; (126°) at 50 mm.; (146°) at 100 mm.; (215°) at 760 mm. S.G. $\frac{0}{4}$ ·765; $\frac{15}{4}$ ·755; $\frac{100}{4}$ ·693. Formed by reduction of lauric acid or of dodecyl alcohol with HI and P (Krafft, *B.* 15, 1698; 16, 1719); *v. also* BROMO-DODECANE.

Dodecane $C_{12}H_{26}$. *Dihexyl.* (201°). S.G. ^{17} ·774. Formed, together with hexane, by treating *sec*-hexyl iodide with Zn and HCl or with sodium, and by the electrolysis of potassium heptoate (Schorlemmer, *A.* 161, 277; Wahl, *B.* 13, 210).

DODECENOIC ACID $C_{12}H_{22}O_2$. *Amenyl-amyl-acetic acid.* One of the substances obtained by passing CO over a mixture of sodium acetate and sodium isoamylate at 180° (Poetsch, *A.* 218, 75). Liquid.

Methyl ether MeA′. (240°–250°).

DODECINENE $C_{12}H_{22}$. (190°–200°). From diallyl by combination with HI and treatment of the resulting $C_6H_{12}I_2$ with an alloy of tin and sodium (Wurtz, *Bl.* [2] 2, 164).

Dodecinene $C_{12}H_{22}$. [c. 9°]. (105°) at 15 mm. S.G. $\frac{0}{4}$ ·8030; $\frac{32}{4}$ ·7788. From di-bromo-dodecane $C_{12}H_{24}Br_2$ and alcoholic KOH at 150° (Krafft, *B.* 17, 1372).

Dodecinene $C_{12}H_{22}$. Possibly *tri-methyl-propyl-benzene tetrahydride.* (211°). From anethol $C_6H_4(OMe).C_3H_5$ and HI at 260° (Landolph, *B.* 9, 725).

DODECOIC ACID *v.* LAURIC ACID.

DODECONENE $C_{12}H_{20}$. (197° i. V.). S.G. $\frac{20}{0}$ ·8385. R_∞ 92·4 (Albitzky, *J. R.* 15, 524). From di-methyl-allyl-carbinol (hexenyl alcohol) and diluted H_2SO_4 at 100° (Nikolsky a. Saytzeff, *J. pr.* [2] 27, 380; 34, 475). Chromic mixture oxidises it with formation of acetone, acetic acid, propionic acid, an acid $C_{10}H_{16}O_6$, which may be $(CH_3)_2C(OH).C(OH)(CO_2H).C(CH_3)_2.CH_2.CO_2H$, and other bodies. Combines with bromine HCl at 100° forms oily $C_{12}H_{21}Cl$.

Dodeconene $C_{12}H_{20}$. (170°–180°). From mesitic ether $C_{12}H_{20}O$ and $ZnCl_2$ (Baeyer, *A.* 140, 301).

Dodeconene $C_{12}H_{20}$. *Diphenyl decahydride.* (225°). From carbazole $C_{12}H_9N$ by treatment with HI and P at 330° (Graebe a. Glaser, *A.* 163, 357).

n-prim-**DODECYL ALCOHOL** $C_{12}H_{25}.OH$. [24°]. (143°) at 15 mm. S.G. (liquid) $\frac{24}{4}$ ·8309; $\frac{40}{4}$ ·8201; $\frac{99}{4}$ ·7781. Large silvery plates.

Formation.—Lauric aldehyde (obtained by distilling barium laurate with barium formiate) is reduced with zinc-dust and acetic acid.

Acetyl derivative $C_{12}H_{25}.OAc$. (151°) at 15 mm. Liquid which can be easily solidified (Krafft, *B.* 16, 1718, 3018).

Palmityl derivative $C_{28}H_{56}O_2$. [42°]. Large plates.

Dodecyl alcohol $C_{12}H_{25}OH$. (265°–275°). From isoamyl isovalerate and sodium (Lourenço a. Aguiar, *Z.* 1870, 404).

DODECYL CHLORIDE $C_{12}H_{25}Cl$. (c. 244°). S.G. ^{22} ·933. Got by chlorinating dodecane from petroleum (Pelouze a. Cahours, *A. Ch.* [4] 1, 5).

n-**DODECYLENE** $C_{12}H_{24}$ *i.e.* $CH_3(CH_2)_9CH:CH_2$. [−31°]. (96°) at 15 mm. S.G. $\frac{0}{4}$ ·7729; $\frac{15}{4}$ ·7620; $\frac{30}{4}$ ·7511. Colourless liquid. Formed by the decomposition of dodecyl palmitate on distillation (Krafft, *B.* 16, 3020; 17, 1371).

Dodecylene $C_{12}H_{24}$. *Tri-isobutylene.* (176°). V.D. (air = 1) 5·64. S.G. ^{0} ·774. Tertiary butyl iodide reacts with ZnO at 15° with separation of water, and on fractional distillation the oily product tri-iso-butylene is got: $6(Me_3CI) + 3ZnO = 3ZnI_2 + 3H_2O + 2C_{12}H_{24}$ (L. Dobbin, *C. J.* 37, 241). It is also formed, along with di-isobutylene, by heating a saturated solution of isobutylene in tertiary butyl iodide with CaO at 100° (Lermontoff, *A.* 196, 116). Formed also by treating isobutylene with H_2SO_4 (Goriainoff a. Butlerow, *B.* 6, 561; *A.* 169, 146; *J. R.* 11, 198).

Properties.—Liquid. Slowly absorbs atmospheric oxygen. Combines with bromine. Chromic mixture forms tri-methyl-acetic, methyl-di-isobutyl-acetic, and acetic acids.

Dodecylene $C_{12}H_{24}$. (213° cor.). S.G. ^{0} ·836. Got by distilling the potash-soap derived from herring oil (Warren a. Storer, *Z.* 1868, 230).

Dodecylene $C_{12}H_{24}$. (208°–215° cor.). In petroleum from Burmah (W. a. S.).

Dodecylene $C_{12}H_{24}$. *Dihexylene.* (c. 198°). S.G. ^{0} ·809; ^{12} ·798. Formed by the action of H_2SO_4 (2 pts.) and water (1 pt.) on methyl-di-ethyl-carbinol (hexyl-alcohol) at −18° (Jawein, *A.* 195, 261).

Dodecylene $C_{12}H_{24}$. *Dodecanaphthene.* (197°). S.G. ^{14} ·806; ^{20} ·801. Occurs in petroleum of Baku (Markownikoff a. Ogloblin, *J. R.* 15, 338).

Dodecyiene $C_{12}H_{24}$. *Dihexylene.* (c. 195°). S.G. ^{0} ·795; ^{12} ·786. From di-methyl-ethyl-ethylene (hexylene) and H_2SO_4 (Jawein, *A.* 195, 261).

DODECYLENE BROMIDE *v.* DI-BROMO-DODECANE.

DODECYLENE GLYCOL *v.* Di-oxy-dodecane.

DODECYLIDENE *v.* Dodecinene.

DOEGLIC ACID $C_{19}H_{36}O_2$. The chief acid produced by the saponification of the train oil obtained from the bottle-nosed whale found near the Faroe Isles (Scharling, *J. pr.* 43, 257). Solidifies a little above 0°.—BaA'_2.—EtA'.

n-**DO-ICOSANE** $C_{22}H_{46}$. [45°]. (225°) at 15 mm. S.G. $^{80}_{4}$ ·755; $^{100}_{4}$ ·742. Formed by reduction of the dichloride of the ketone obtained by distilling a mixture of barium palmitate and heptoate (Krafft, *B.* 15, 1718; 21, 2256). Present also in paraffin derived from bituminous shale by distillation.

DOTRIACONTANE *v.* Dicetyl.

DOUBLE SALTS. By a salt was meant in the early days of chemistry a solid substance e. sol. water and re-obtainable by evaporating its aqueous solution. When the composition and modes of formation of bodies with these properties came to be examined, it was found that many of them were formed by the interaction of an acid with an alkali, and were composed of the elements of the acid and the alkali. Hence the study of salts carried with it the study of acids and alkalis. Acids and alkalis were at first described as compounds with certain characteristic properties, rather physical than chemical (*v.* Acids and Alkalis); the more accurate study of these bodies showed that all acids are composed of hydrogen combined with a strongly negative element or elements, and that all alkalis are compounds of markedly positive metals with hydrogen and oxygen. By the interaction of an acid and an alkali a salt is formed; the salt is not characterised by the properties either of the acid or the alkali; the salt is composed of the metal of the alkali combined with the more negative part of the acid. Then it was found that salts could be formed in other ways than by the interaction of acid and alkali; but, however formed, the salt is a compound of a positive element (a metal) with a negative element or group of elements.

A salt may, then, be described either as a derivative of an acid obtained by exchanging the whole or a portion of the hydrogen of the acid for metal, or as a compound of two radicles, one positive and the other negative. If the latter form of description is adopted, the positive radicle of the salt may generally be regarded either as a metal or as a group composed of a metal and non-metal, the non-metal being usually oxygen, and the negative radicle may be regarded as either a non-metal or a group composed of negative elements. The following formulæ represent the composition of some salts:—

Salt.	Composition of salt when regarded as (1) *derivative of an acid.*	 (2) *compound of two radicles.*
KNO_3	$K.NO_3$ (acid = HNO_3)	$K_2O.N_2O_5$ (= $2KNO_3$)
K_2SO_4	$K_2.SO_4$ (acid = H_2SO_4)	$K_2O.SO_3$
$KHSO_4$	$K.HSO_4$ (acid = H_2SO_4)	$K_2O.2SO_3.H_2O$ (= $2KHSO_4$)
$AlPO_4$	$Al.PO_4$ (acid = H_3PO_4)	$Al_2O_3.P_2O_5$ (= $2AlPO_4$).

There are many salts which cannot well be formulated as derived from acids by replacing hydrogen by a metal, but rather as compounds of such salts with the oxide, or hydroxide, of the replacing metal. As instances of these *basic salts* may be mentioned $Bi(NO_3)_3.Bi_2O_3$ and $PbC_2H_3O_2.Pb(OH)_2$. Such salts may, however, be formulated as compounds of two radicles, one negative and the other positive; thus $3Bi_2O_3.3N_2O_5 = 2[Bi(NO_3)_3.Bi_2O_3]$, $2PbO.C_2H_3O.H_2O = PbC_2H_3O_2.Pb(OH)_2$.

Some salts are composed of two metals combined with an acidic radicle or radicles; so far as composition is concerned these *double salts* may be regarded either as derived from an acid or from two acids, by exchanging hydrogen for two metals, or as composed of two positive radicles combined with a negative, or with two negative, radicles. They may also be formulated as compounds of two salts. The following examples will illustrate these conceptions of *double salts*:—

Double salt.	Composition of salt when regarded as I. *Derivative of acid or acids.*	 II. *Composed of radicles.*	 III. *Composed of two salts.*
$Al_2K_2S_4O_{16}$	$Al_2K_2.4SO_4$ (acid = H_2SO_4)	$Al_2O_3.K_2O.4SO_3$	$Al_2(SO_4)_3.K_2SO_4$.
$MgNa_2C_2O_6$	$MgNa_2.2CO_3$ (acid = H_2CO_3)	$MgO.Na_2O.2CO_2$	$MgCO_3.Na_2CO_3$.
$Cd(NH_4)_4Cl_6$	$Cd(NH_4)_4.6Cl$ (acid = HCl)	$Cd.4NH_4.6Cl$	$CdCl_2.4NH_4Cl$.
$Hg_2CaCy_2Cl_2$	$Hg_2Ca.Cy_2Cl_2$ (acids = HCy and HCl)	$Hg_2.Ca.Cl_2Cy_2$	$HgCy_2.CaCl_2$.
$HgAgCy_2NO_3$	$HgAg.Cy_2NO_3$ (acids = HCy and HNO_3)	$Hg.Ag.Cy_2NO_3$	$HgCy_2.AgNO_3$.

To this class of *double salts* also belong compounds composed of a single metal combined with two acidic or negative radicles, thus:—

$Hg_2I_2SO_4$	$Hg_2.I_2SO_4$ (acids = H_2SO_4 and HI)	$Hg_2.I_2SO_4$	$HgI_2.HgSO_4$.

The most generally applicable way of looking at double salts, when attention is paid solely to composition, is evidently to regard them as composed of two salts. All double salts will thus be brought within the general formula $xM.yN$, where M is one salt and N another. But if the constitution of the double salts is to be understood, and the salts are to be classified, attention must be paid not only to their composition but also to their properties. Some double salts interact with various reagents as chemical wholes; thus the body $FeCy_2.4KCy$ reacts with acids to give the acid H_4FeCy_6 and a salt of K; so also it reacts with many metallic salts in solution to give pps. of the composition $M^{I}_4FeCy_6$ or $M^{II}_2FeCy_6$, where M^{I} is a monovalent, and M^{II} a divalent, metal. The double salt in question is therefore regarded as the K salt of the acid H_4FeCy_6, and its formula is written K_4FeCy_6, a formula which is strictly conformable with $FeCl_3$, $Fe(NO_3)_3$, $Fe_2(SO_4)_3$, and other formulæ of simple salts. Other double salts interact with various reagents as if they were composed of two simple salts; thus, AgCy.KCy reacts with acids to produce HCy, a salt of Ag, and a salt of K. Other double salts react with some reagents in one way, and with others in another way; for instance, $HgCy_2.2KCy$ is decomposed by acids with evolution of HCy, but an aqueous solution of this double salt reacts with lead or zinc salts to form a pp. of $HgCy_2.PbCy_2$ or $HgCy_2.ZnCy_2$, respectively. In the latter changes the double salt $HgCy_2.2KCy$ reacts as if it were K_2HgCy_4.

A slight extension of the application of the conception of compound radicles is probably sufficient to bring the double salts within the generally accepted notions of chemical constitution. If we examine a few reactions of a specified compound, we may arrive at a conception of its constitution which finds expression in a structural formula representing the compound as built up of certain radicles. But a more exhaustive study of the same compound may lead to another structural formula. Thus, the formulæ $H.C_2H_3O_2$, $C_2H_3O.OH$, and $CH_3.COOH$ mark successive advances in the chemical study of acetic acid. The third formula is the best, because it suggests more reactions than either of the others. In the case of such a compound as acetic acid we cannot actually build up the compound from the radicles which we represent in the formula. But we are generally able to build up a double salt by bringing together two simple salts; hence we are apt to think that the atomic complex which forms the reacting unit of the salt must be composed of these two radicles which have actually been caused to combine. This may not, however, be the proper view to take of the constitution of the salt; whether it is or is not the proper view can be determined only when an exhaustive study has been made of the reactions of formation and decomposition of the compound. But as most double salts have only been superficially examined, our present conceptions of the constitution of these bodies cannot be regarded as final. In connexion with the subject of double salts *v.* article Salts. M. M. P. M.

DRAGON'S BLOOD. A red resin. American dragon's blood flows from incisions in *Pterocarpus draco* growing in the West Indies. A similar resin is obtained from *Croton draco.* Indian dragon's blood is found on the ripe fruits and leaves of various species of *Calamus.* Canary dragon's blood comes from *Dracæna draco.* It dissolves in alcohol, ether, and oils, forming a red solution. It is partially soluble in alkalis (Johnstone, *Tr.* 1839, 134; Herberger, *Buchn. Repert.* 37, 17; 40, 138). According to Dobbie a. Henderson (*Ph.* [3] 14, 361) these resins may be arranged in four groups:—

(*a*) Sol. $CHCl_3$, CS_2, and benzene.
(*b*) Sol. $CHCl_3$, insol. CS_2, and benzene.
(*c*) Sol. $CHCl_3$, partly sol. CS_2, sol. benzene.
(*d*) Insol. $CHCl_3$, CS_2, and benzene.

The other properties of these resins are somewhat dissimilar:—

(*a*) $C_{18}H_{18}O_4$. [80°]. From *Calamus draco.*
(*b*) $C_{17}H_{19}O_5$. [c. 100°].
(*c*) $C_{18}H_{18}O_4$. [c. 80°]. From dracæna.

The following properties probably relate chiefly to the resin from *Pterocarpus draco*:—

On dry distillation it gives toluene and styrene (Glénard a. Boudault, *C. R.* 17, 503; 19, 505; Blyth a. Hofmann, *A.* 53, 326). Potash-fusion forms benzoic acid, *p*-oxy-benzoic acid, and phloroglucin (Hlasiwetz a. Barth, *A.* 134, 283). Distillation with zinc-dust gives a large quantity of styrene, together with toluene, ethyl-benzene, and three oils, $C_{11}H_{16}O$ (215°) V.D. 5·5, $C_{13}H_{20}O$ (258°) V.D. 6·96, and $C_{16}H_{20}O_2$ (238°) (Bötsch, *M.* 1, 609).

DRUPOSE *v.* Sugar.

DUALISM. As the study of chemical composition was developed by Lavoisier, Dalton, Davy, Berzelius, and others, chemists gradually drew a marked line of distinction between two classes of compounds, those namely which when dissolved in water had a sour taste, dissolved metals, corroded animal matter, and changed the colour of some vegetable substances from blue to red, and those whose aqueous solution had a soap-like action on the skin, did not dissolve metals, and restored the colour of the vegetable substances which were altered by the first class of compounds. But these two groups of compounds comprised a minority of the bodies which it was the business of chemistry to investigate. There were very many substances which did not possess the characteristics of either class; as investigation proceeded it was discovered that the greater number of the members of the intermediate class could be produced by the interaction of bodies belonging to one of the extreme classes with bodies belonging to the other. Compounds belonging to the first class were called acids, the second class was named bases or alkalis, and a compound formed by the mutual action of an acid and a base was called a salt.

The mode of production of salts suggested the view that these compounds are built up of two parts, one of which has the characters of an acid, and the other the characters of a base. This view was confirmed by the results of the electro-chemical researches of Davy and Berzelius. The passage of an electric current through a salt very frequently produced one body having the characters of an acid, and another having the properties of a base. Berzelius supposed that every salt is essentially composed of two parts, one of which is electrically positive to the other; in some cases each part or radicle of a salt is itself an element, in other cases each part is itself a group of elements.

Having expounded his view of chemical action as an electrical phenomenon essentially consisting in the attraction of one body, either elementary or compound, by another with an electrical polarity stronger than that of the first, Berzelius proceeds thus:—

> 'If these electro-chemical conceptions are just, it follows that every chemical compound is dependent on two opposing forces, positive and negative electricity, and on these alone; and that every compound must be composed of two parts held together by their mutual electro-chemical reactions. Therefore it follows that every compound body, whatever be the number of its constituents, can be separated into two parts, whereof one is positively and the other negatively electrified. Thus, for example, sodium sulphate is put together, not from sulphur, oxygen, and sodium, but from sulphuric acid and soda, which again can themselves be separated into positive and negative constituents. So also alum cannot be regarded as immediately built up from its elements, but must rather be looked on as the product of a reaction between sulphate of alumina and sulphate of potash, the former acting as a negative, the latter as a positive element.'—*Lehrbuch* (1st ed.), 3, pt. i. 77.

This is the doctrine of *dualism*, a doctrine which prevailed in chemistry for something like half a century. As soon as a new salt was prepared, the dualistic chemist set himself to construct a formula which should represent the salt as composed of two parts, or radicles, one positive and the other negative. The formula given to the same salt was not always the same; but in whatever way the formula was modified, in accordance with the known reactions of the salt, the fundamental conception of binary structure remained. The following formulæ, among others, were given at different times to sodium acetate—(C = 6, O = 8):—

$C_4H_3NaO_3.H_2O$
$C_4H_3NaO_4.H_2$
$(C_2H_3Na)C_2O_3.H_2O$
$C_4H_7Na.O_4$
$C_4H_5NaO_2.H_2O_2$

The conception on which dualism was based, the conception, namely, of binary structure, was extended to acids and bases; every acid and every base was regarded as composed of two radicles, one of which was frequently, but not always, an element. A complete system of chemical classification was thus developed: one element combines with another; the compound is evidently a binary one; the compound interacts with another binary compound; the product is still binary although each part is itself a compound; the new compound enters into chemical union with a compound as complex as itself; the product is still essentially built up of two parts. Each elementary atom was regarded by Berzelius as endowed with both positive and negative electricity, but one of these predominated over the other, so that the atom, considered as a whole, was either negatively or positively electrified. When a positively electrified atom combined with one which was negatively electrified, Berzelius said that opposite electricities neutralised each other, but, he added, the electricities formerly masked in the separate atoms now come into play, so that the new group of atoms, considered as a whole, is either positively or negatively electrified, and in virtue of this the new group of atoms is ready to combine with other atoms or groups of atoms, provided the predominating electricity on these is of opposite sign to that on the first group. As compounds become more complex the less readiness do they exhibit to enter into fresh combinations; this was accounted for by Berzelius as a consequence of the neutralisation of the predominating or stronger electricities by the first combination of the elementary atoms. Suppose an atom to have a large charge of positive and a small charge of negative electricity, and suppose this atom to come within the sphere of action of another having a large charge of negative and a small charge of positive electricity; these atoms will have a great affinity for each other—according to the Berzelian doctrine of dualism—they will combine, and the compound will be either positively or negatively electrified, but the total charge will be considerably smaller than that on the original atoms.

Chemical affinity was regarded by the Berzelian school as conditioned by, if not as synonymous with, greater or smaller electrical charges. Suppose that a series of binary compounds has been produced, one of these being very stable, another less stable, another unstable, and so on, the electrical charges on the atoms of the most stable compound must have been greater than the charges on the atoms of the less stable compounds; therefore a greater quantity of electricity will be required to tear asunder the atoms which form the most stable compound than is required to decompose an equivalent quantity of one of the less stable compounds. But Faraday's researches on electrolysis showed that the passage of the same quantity of electricity through a series of electrolytic compounds of varying chemical stability resulted in the decomposition of chemically equivalent masses of these compounds. This result was opposed to the dualistic conception of affinity, and hence to the whole system of dualism.

The researches of Liebig and Graham on the constitution of acids gradually led chemists to regard these bodies as essentially compounds of hydrogen with negative elements or groups of elements; they came to look on the reaction between an acid and a metal as consisting in the replacement of part, or the whole, of the hydrogen of the acid by the metal, and they recognised that the hydrogen of some acids could be replaced by metal in two, three, or more, successive stages. An acid thus came to be regarded as a whole, the functions of the parts of which depend on the nature of these parts, and probably on their arrangement relatively to each other. But the dualistic chemist asserted that hydrogen belongs to the class of metals, because both are distinctly positive elements, and he maintained that the replacement of one positively electrified atom by another positively electrified atom might be expected to result in the production of a compound resembling the original; the acid type is preserved, he asserted, when a salt is formed by putting a metal in the place of the hydrogen of an acid; both acid and salt are dualistic structures of the same kind. It is impossible, asserted the follower of Berzelius, to replace the strongly positive hydrogen in a compound by a distinctly negative element without producing a compound of an entirely different type from the acid; a negative element, such as chlorine, cannot, he said, be put in the place of the positive element hydrogen; if hydrogen is removed and a compound containing chlorine is formed, this process must consist in the breaking down of one dualistic structure and the formation of another totally unlike the first. But in 1839 Dumas prepared trichloracetic acid and proved this compound to be very similar to acetic acid, although it was produced by replacing three atoms of hydrogen in acetic acid by three atoms of the markedly negative element chlorine (*C. R.* 8, 609). Dumas retained the notion of types or families; but he said that compounds were to be placed in this or that family, because of their actual reactions of formation and decomposition, and not because a certain hypothesis required them to be classified in a certain way.

Dualism had paid too exclusive attention to composition; Dumas, and the founders of the *unitary hypothesis*, maintained that no chemical classification can be approximately final which does not endeavour to study the properties as well as the compositions of the bodies to be classified (*v.* Classification; also Salts, and Types). M. M. P. M.

DUBOISINE. Identical with Hyoscyamine (*q. v.*).

DULCAMARIN $C_{22}H_{34}O_{10}$. Occurs in the stalks of the common nightshade, *Solanum dulcamara* (Wittstein, *Vierteljahrb. f. pr. Pharm.* 1, 364, 495; E. Geissler, *Ar. Ph.* [3] 7, 289). Amorphous, with bitter taste followed by a persistent sweet taste. Sol. alcohol and acetic ether. Basic lead acetate ppts. $C_{22}H_{32}PbO_{10}$ 3aq and $C_{22}H_{32}PbO_{10}$ 5aq. Dilute acids resolve it into glucose and resinous dulcamaretin $C_{16}H_{26}O_6$.

DULCITE $C_6H_{14}O_6$ *i.e.* $CH_2(OH).(CH.OH)_4.CH_2OH$. *Melampyrite.* Mol. w. 182. [189°]. S.G. $\underline{15}$ 1·466. S. 3 at 15°. S. (alcohol) ·07 at 15°. H.F. 294,000 (v. Rechenberg); 317,600 (Berthelot a. Vieille, *A. Ch.* [6] 10, 456; *Bl.* [2] 47, 868). H.C.v. 729,100; H.C.p. 729,400 (B. a. V.).

Occurrence.—In Madagascar manna (Laurent, *Compt. Chim.* 1850, 364; 1851, 29; *A.* 76, 358; 80, 345; Jacquelain, *Compt. Chim.* 1851, 21; *A.* 80, 345). In *Melampyrum nemorosum* (Hünefeld, *J. pr.* 7, 233; 9, 47; *A.* 24, 241; Gilmer, *A.* 123, 372); in *Scrophularia nodosa* and *Rhinanthus Crista-galli* (Eichler, *Rep. Chim. pure*, 2, 103); and in the cambial cells of *Euonymus europæus* (Kubel, *J. pr.* 85, 372).

Formation.—By reducing galactose or milk sugar with sodium amalgam (Bouchardat, *A. Ch.* [4] 27, 68; *C. R.* 83, 199; 84, 665, 866, 1406; *Bl.* [2] 18, 115).

Preparation.—1. From Madagascar manna by recrystallisation.—2. The decoction from *Melampyrum nemorosum* is boiled with addition of milk of lime, and the solution concentrated; the hot solution is acidified with HCl, and on cooling dulcite crystallises out (Eichler).

Properties.—Glittering monoclinic prisms, usually aggregated in crusts. Slightly sweet in taste. Inactive. Sl. sol. acetone, chloroform, and acetic ether, insol. ether. It does not reduce Fehling's solution. Does not undergo alcoholic fermentation. At 200° it loses water, becoming dulcitan $C_6H_{12}O_5$, a thick syrup. Dulcite is neutral to litmus, but according to Klein (*C. R.* 99, 144) a solution of dulcite (1 mol.) mixed with borax (½ mol.) is acid. Sodium paratungstate acts like borax.

Reactions.—**1.** Boiling dilute *nitric acid* forms mucic, racemic, and oxalic acids (Laurent; Carlet, *C. R.* 51, 137; 53, 343). Fuming HNO_3 forms the hexanitrate.—**2.** H_2SO_4 forms a pentasulphuric acid.—3. HI forms secondary hexyl iodide (Erlenmeyer a. Wanklyn, *C. J.* 15, 455).—4. Conc. HClAq at 0° forms unstable crystals of $C_6H_{14}O_6HCl$ 3aq (Bouchardat, *A. Ch.* [4] 27, 168).—5. HClAq at 100° slowly forms the dichlorhydrin $C_6H_{12}Cl_2O_4$. This forms tables, insol. water and alcohol; it is split up at 180°, or by boiling water, into HCl and dulcitan chlorhydrin $C_6H_{11}ClO_4$, which crystallises from ether in needles [90°], and is partially converted by boiling water into dulcitan. The dichlorhydrin is converted by alcoholic NH_3 into dulcitamine $C_6H_{13}NO_5$, a strongly alkaline syrup which absorbs CO_2 from the air and forms a crystalline hydrochloride B′HCl and platinochloride $B'_2H_2PtCl_6$. Sodium amalgam converts dulcite dichlorhydrin into gummy dulcide $C_6H_{12}O_4$. Fuming HNO_3 gives $C_6H_8Cl_2(NO_3)_4$ [108°]. 6. HBr gives $C_6H_{14}O_6HBr$ 3aq, $C_6H_{12}Br_2O_4$, and $C_6H_{11}BrO_4$ [143°] under conditions similar to those under which the corresponding chlorine derivatives are formed. The prolonged action of a large excess of HBrAq at 100° forms syrupy $C_6H_8Br_4O$. Dulcitan chlorhydrin is converted by HBrAq at 100° into crystalline $C_6H_{12}ClBrO_4$. Dulcite dibromhydrin is converted by fuming HNO_3 into $C_6H_8Br_2(NO_3)_4$ [100°]; while $C_6H_{12}ClBrO_4$ gives $C_6H_8ClBr(NO_3)_4$ [115°].—7. HIAq (S.G. 2·0) at 15° forms $C_6H_{14}O_6HI$ 3aq, which is completely resolved into its components by water.—8. Boiling AcCl forms $C_6H_8Cl(OAc)_5$, which forms minute crystals.—9. Ac_2O forms several acetyl derivatives (*v. infra*). Butyric acid at 200° gives oily di-butyryl dulcitan $C_6H_{10}(C_4H_7O)_2O_5$.—10. If *bromine* (5 g.) be added to a solution of dulcite (5 g.) in water (40 g.) containing Na_2CO_3 (12 g.), and the product subsequently tested with phenyl hydrazine, the phenyl hydrazide $C_{18}H_{22}N_4O_4$ [206°] of an aldehyde or ketone ('phenyl dulcitosazone') separates as yellow flakes (Fischer a. Tafel, *B.* 20, 3384).—11. By heating dulcite with *phenyl cyanate* there is formed $C_6H_8(OH)(O.CO.NHPh)_5$ [c. 252°], very sparingly soluble in all solvents (Tessmer, *B.* 18, 971).

Metallic compounds.—$C_6H_{12}BaO_6$ 8aq: prisms, v. sol. warm water.—$C_6H_8Pb_3O_6$ 3aq (at 100°).—$C_6H_8Cu_3O_6$ 3aq (at 100°).

Hexanitrate $C_6H_8(NO_3)_6$. *Nitrodulcite.* [c. 70°]. From dulcite (1 pt.), fuming HNO_3 (5 pts.), and H_2SO_4 (10 pts.), the mixture being immediately thrown into water (Béchamp, *C. R.* 51, 257; Champion, *Bl.* [2] 22, 179). Colourless flexible needles (from alcohol). When kept for a month at 30° to 45° it evolves red fumes, and apparently changes to the tetranitrite $C_6H_8(OH)_2(NO_2)_4$ [130°–140°], which crystallises from alcohol in prisms.

Tri-sulphuric acid $C_6H_8(SO_4H)_3(OH)_3$. From dulcite and H_2SO_4 (Eichler).—$Ba_3A'''_2$: gummy.

Penta-sulphuric acid $C_6H_8(SO_4H)_5(OH)$. When dulcite is added in small portions to chlorosulphuric acid ($ClSO_4H$), and the product is dissolved in water, a solution is obtained whence a barium salt may be got in the form of a hygroscopic powder. Writing ba for ½Ba, it is either $(baSO_4)_5C_6H_8(OH)$, 2aq or $(baSO_4)_5C_6H_7$, 3aq. The latter formula represents it as derived from dulcitan, and, in fact, if the free acid is heated on the water-bath dulcitan is produced (Claesson, *J. pr.* 128, 15).

Di-acetyl derivative $C_6H_8(OH)_4(OAc)_2$. [176°]. From boiling Ac_2O (12 pts.), HOAc (120 pts.), and dulcite (10 pts.) (Bouchardat). Scales. Sl. sol. cold water, insol. ether. A by-product is diacetyl dulcitan $C_6H_{10}Ac_2O_5$, a bitter substance, sol. water and ether.

Penta-acetyl derivative $C_6H_8(OH)(OAc)_5$. [163° cor.]. From $C_6H_8Cl(OAc)_5$ by boiling with alcohol. Needles.

Hexa-acetyl derivative $C_6H_8(OAc)_6$. [171° cor.]. From dulcite (1 pt.), Ac_2O (5 pts.), and HOAc at 185°. Hard crystalline plates; sublimes at 210°. A by-product in its preparation is tetra-acetyl-dulcitan $C_6H_8O(OAc)_4$, an insupportably bitter resin.

Hexa-benzoyl derivative $C_6H_8(OBz)_6$. [147°]. From dulcite (1 mol.) and BzCl (8 mols.) at 150°–200°. Crystals (from alcohol), insol. water and ether. HNO_3 mixed with H_2SO_4 convert it into $C_6H_8(O.CO.C_6H_4NO_2)_6$. Tetra-benzoyl-dulcitan $C_6H_8O(OBz)_4$ is a resin formed as a by-product in preparing hexa-acetyl-dulcite.

Isodulcite $C_6H_{14}O_6$ or $C_6H_{12}O_5$ aq. *Rhamnose.* [92°]. S.G. $\frac{20}{4}$ 1·471. S. 56·7 at 18°; 109 at 40°. $[\alpha]_D = 8·07°$ in a 21 p.c. aqueous solution at 17°; $[\alpha]_D = 13°$ in fresh solutions (Rayman a. Kruis, *C. C.* 1888, 6). Prepared by the action of dilute H_2SO_4 upon quercitrin (the yield being 10 p.c., Hlasiwetz a. Pfaundler, *A.* 127, 362), upon the glucoside of buckthorn berries (*Rhamnus infectoria*) Liebermann a. Hörmann, *B.* 11, 952; Berend, *B.* 11, 1353), and upon sophorin (Förster, *B.* 15, 215). Monoclinic crystals, sol. water and alcohol. In very dilute alcoholic solutions it is lævorotatory, in concentrated alcoholic and in aqueous solution it is dextrorotatory. 10 c.c. of Fehling's solution, equivalent to ·05 g. glucose, are reduced by ·055 g. isodulcite (Will, *B.* 18, 1316). Isodulcite also reduces ammoniacal silver nitrate, Knapp's reagent, an alkaline solution of indigo, an alkaline solution of K_3FeCy_6, and picric acid (to picramic acid). It does not affect Schiff's reagent. H_2SO_4 dissolves it unchanged. Does not undergo alcoholic fermentation with yeast. At 100° it gives off H_2O becoming $C_6H_{12}O_5$, sometimes called **isodulcitan**, which takes up H_2O again on dissolving in water.

Reactions.—1. *Potash* and *iodine* give a very little iodoform.—2. (α)-*Naphthol* and H_2SO_4 give a bluish-violet colour.—3. *Thymol* and H_2SO_4 give a crimson zone rapidly turning brown.—4. *Phenyl hydrazine* mixture gives a heavy pp. $C_6H_{10}O_4(N_2HPh)_2$ or $C_{18}H_{22}N_4O_3$ [171°] sl. sol. water, v. sol. alcohol (Rayman, *Bl.* [2] 47, 668; Herzog, *M.* 8, 227).—4. Heated with phenyl-hydrazine in alcoholic solution it gives a phenyl-hydrazide $C_{12}H_{18}N_2O_4$ or $C_6H_{12}O_4(N_2HPh)$ [159°] v. sl. sol. alcohol (Rayman, *Bl.* [2] 47, 760; Fischer a. Tafel, *B.* 20, 2566).—5. A mixture of H_2SO_4 and HNO_3 forms a very unstable explosive **nitrate** $C_6H_9(NO_3)_3O_2$.—6. Moist *silver oxide* oxidises isodulcite to acetic acid. CrO_3 does the same. *Bromine* followed by Ag_2CO_3 oxidises it to $C_6H_{10}O_5$ [148°] (Will a. Peters, *B.* 21, 1813), or [142°] (Rayman, *B.* 21, 2046). This 'isodulcite saccharin' forms needles, v. sol. water and alcohol, sl. sol. ether; $[\alpha]_D = -39°$; S.G. $\frac{15}{4}$ 1·0325; S. 11.—7. Aqueous NaOH and BzCl form a crystalline mixture of tri- and tetra-benzoyl derivatives.—8. Ac_2O at 120°–140° forms resinous acetyl derivatives.

Sodium salt $C_6H_{12}Na_2O_6$. From isodulcite and alcoholic NaOEt (Liebermann a. Hamburger, *B.* 12, 1186). Crystalline powder.

Isodulcite carboxylic acid $C_7H_{14}O_7$. ***Lactone*** $C_7H_{12}O_6$. [168°]. Formed by heating isodulcite (25 g.) dissolved in water (25 c.c.) with anhydrous HCy (7·5 c.c.) at 30°; and subsequent saponification (Fischer a. Tafel, *B.* 21, 1657; 2173). Concentrically grouped needles, v. sol. water and alcohol, v. sl. sol. ether. Reduced by HI and P to *n*-heptoic acid.

ISODULCITIC ACID $C_6H_{10}O_8$. [100°]. Formed by oxidising isodulcite with HNO_3 (S.G. 1·33) (Malin, *A.* 145, 197). Crystalline grains, v. sol. water, v. sl. sol. alcohol. Does not reduce Fehling's solution. — $C_6H_6Pb_2O_8$. — $C_6H_8CdO_8$ (at 120°). — $C_6H_8BaO_8$ (at 120°): white pp. — $C_6H_8CaO_8$ (at 120°).

ISO-DULCITONIC ACID $C_6H_{12}O_6$×.

Formation.—By oxidising isodulcite with bromine the lactone of isodulcitonic acid is formed. This is converted into salts of the acid by boiling with the respective carbonates (Will a. Peters, *B.* 21, 1814).

Properties.—The free acid is not known. When liberated from the salts it is always the lactone [148°] which is ppd.

DUMASIN $C_9H_{14}O$ (Kane); $C_6H_{10}O$ (Heintz, *P.* 68, 279; Fittig, *A.* 110, 21). V.D. 5·2 (Kane). One of the products obtained by passing acetone or acetic acid through red-hot tubes (Kane, *P.* 44, 494) or by the rapid distillation of acetates. Oil. Lighter than water. Resembles mesityl oxide. Combines with $NaHSO_3$ the crystalline compound $C_6H_{10}ONaHSO_3$ 2aq being decomposed by boiling water. On distillation with MnO_2 and HCl it gives $C_6H_8Cl_2O$ (150°–155°).

DUODECANE *v.* DODECANE.

DURENE $C_{10}H_{14}$ *i.e.* $C_6H_2(CH_3)_4$ [1:2:4:5]. *s-Tetra-methyl-benzene.* Mol. w. 134. [81°]. (196° i. V.).

Occurrence.—In the fraction 170°–180° of coal-tar oils (Schulze, *B.* 18, 3032; *cf.* Berthelot, *Bl.* [2] 8, 226).

Formation.—1. From bromo-ψ-cumene [71°], MeI, and Na (Jannasch a. Fittig, *Z.* 1870, 161; Nef, *A.* 237, 3; Gattermann, *A.* 244, 56).—2. From di-bromo-*m*-xylene MeI, and Na (Jannasch, *B.* 7, 692; Gissmann, *A.* 216, 201). Similarly from di-bromo-*p*-xylene (Jannasch, *B.* 10, 1357).—3. By the action of MeCl in presence of Al_2Cl_6 upon toluene, *o*- or *p*- xylene, or ψ-cumene (Friedel a. Crafts, *A. Ch.* [6] 1, 461; 11, 270; Ador a. Rilliet, *B.* 12, 331; Jacobsen, *B* 14, 2629).—4. By the action of MeI on a mixture of ψ-cumene, CS_2 and Al_2Cl_6 at 100° (Claus a. Fœcking, *B.* 20, 3097).—5. In small quantity by passing oil of turpentine through a red-hot tube (Montgolfier, *A. Ch.* [5] 19, 164).

Properties.—Monoclinic crystals with faint odour. V. sol. alcohol, ether, and benzene, sl. sol. cold HOAc. May be sublimed.

Reactions.—1. Gives by oxidation pyromellitic acid $C_6H_2(CO_2H)_4$, tri-methyl-benzoic acid $C_6H_2(CH_3)_3(CO_2H)$, di-methyl-benzoic acid $C_6H_2(CH_3)_2(CO_2H)_2$, and acetic acid (Reuter, *B.* 11, 31).—2. By leaving in contact with 10 times its weight of ordinary conc. H_2SO_4 about ¼ of it is converted into a *mono-sulphonic acid.* This sulphonic acid is very unstable, being partially reconverted into durene by cold conc. H_2SO_4. By the prolonged (3 or 4 days') action of conc. H_2SO_4 in the cold or for a shorter time at 80°–100° upon durene or its sulphonic acid a complicated reaction takes place with production of two pseudo-cumene-sulphonic acids $C_6H_2Me_3(SO_3H)$[1:3:4:5] and [1:3:4:2], a sulphonic acid of the (1:2:3:4) tetra-methyl-benzene (prehnitene), and hexa-methyl-benzene. In this remarkable reaction the H_2SO_4 behaves in a similar manner to $AlCl_3$. By the action of cold fuming H_2SO_4 upon durene a disulphonic acid is obtained which is much more stable than the mono-sulphonic acid (Jacobsen, *B.* 19, 1209).—

3. Heated with PCl_5 at 195° it gives a chloride $C_{10}H_{10}Cl_4$ which when treated with water at 175° loses all its chlorine. As there is no acid formed it is probable that this chloride contains neither the group CCl_3 nor the group $CHCl_2$. A chloride $C_{10}H_{11}Cl_3$ may be obtained from the ligroin which serves to purify the $C_{10}H_{10}Cl_4$; it is changed by boiling water into a viscous mass, sl. sol. ether (Colson a. Gautier, *A. Ch.* [6] 11, 30).—4. *Benzoyl chloride* in presence of Al_2Cl_6 at 120° forms phenyl tetra-methyl-phenyl ketone $C_6H_5.CO.C_6HMe_4$ [119°] (343°), and di-phenyl tetra-methyl-phenylene diketone $(C_6H_5CO)_2C_6Me_4$ [270°] (Friedel, Crafts, a. Ador, *C.R.* 88, 880).—5. *Acetyl chloride* and Al_2Cl_6 give $C_6HMe_4.CO.CH_3$ (253° uncor.) which may be oxidised to $C_6HMe_4.CO.CO_2H$ whence sodium-amalgam produces $C_6HMe_4.CH(OH).CO_2H$ [156°] (Claus a. Fœcking, *B.* 20, 3097).

u-**Durene** $C_6H_2(CH_3)_4$ [1:3:4:5]. *Isodurene.* (196° i. V.).

Formation.—1. From bromo-mesitylene, MeI, and sodium (Jannasch, *B.* 8, 356).—2. By the action of $ZnCl_2$ or I on camphor (Armstrong a. Miller, *B.* 16, 2259; Montgolfier, *A. Ch.* [5] 19, 164).—3. By treating penta-methyl-benzene with H_2SO_4 (Jacobsen, *B.* 19, 1216).—4. From mesitylene (or toluene), MeCl, and Al_2Cl_6 (Jacobsen, *B.* 14, 2629; Claus a. Fœcking, *B.* 20, 3097; Friedel a. Crafts, *A. Ch.* [6] 1, 461).

Properties.—Oil. Gives on oxidation mellophanic acid $C_6H_2(CO_2H)_4$ and three acids of the formula $C_6H_2(CH_3)_3CO_2H$.

c-**Durene** $C_6H_2(CH_3)_4$ [1:2:3:4]. *Prehnitene.* [−4°]. (204° i. V.). Obtained by hydrolysis of its sulphonic acid, which is found amongst the products of the action of conc. H_2SO_4 upon *s*-durene (Jacobsen, *B.* 19, 1211). It appears also to be formed by the action of MeI and sodium upon bromo-ψ-cumene (Kelbe a. Pathe, *B.* 19, 1551). Formed also by the action of H_2SO_4 on penta-methyl-benzene (Töhl, *B.* 21, 904). Dilute HNO_3 oxidises it to $C_6H_2(CH_3)_3CO_2H$; more energetic oxidation gives prehnitic acid $C_6H_2(CO_2H)_4$. The picric acid compound crystallises from alcohol in yellow needles [95°]. *c*-Durene forms a di-bromo- derivative [210°], a nitro- derivative [61°], and a di-nitro- derivative [178°].

V. also BROMO-, CHLORO-, and NITRO- DURENES.

Durene dihydride $C_{10}H_{16}$. (166°). In animal oil (Weidel a. Ciamician, *B.* 13, 73). Gives isophthalic acid on oxidation. Successive treatment with bromine and aniline converts it into cymene. The oil appears also to contain an isomeride (172°).

DURENE CARBOXYLIC ACID *v.* TETRA-METHYL-BENZOIC ACID.

DURENE SULPHONIC ACID $C_6HMe_4(SO_3H)$. Obtained from Caucasian petroleum by sulphonation (Markownikoff a. Ogloblin, *A.* 234, 99). Formed, together with its chloride and di-duryl sulphone by treatment of powdered durene with 2½ pts. of $ClSO_3H$ at 0°. Crystalline solid. V. sol. water, but ppd. by H_2SO_4. When left to stand with H_2SO_4 for 12 hours at 50° it is converted into hexa-methyl-benzene, *c*-durene sulphonic acid, and two ψ-cumene sulphonic acids. When distilled with dilute H_2SO_4 hydrolysis begins as soon as, through evaporation of water, the temperature rises to 120° (Armstrong a. Miller, *C. J.* 45, 148). By fusion with KOH it gives durenol [117°].

Salts.—A'Na: pearly rhombic plates; v. sol. hot water, sl. sol. cold water, nearly insol. dilute NaOH.—A'K: thin rhombic plates, sl. sol. cold water.—A'_2Ba: pp. of small scales or rhombic plates, v. sol. hot water.—A'_2Cu: light blue six-sided tables; v. sl. sol. water.

Chloride $C_6HMe_4(SO_2Cl)$: [99°]; glistening prisms; v. e. sol. ether, sl. sol. alcohol at 0°.

Amide $C_6HMe_4(SO_2NH_2)$: [155°]; long prisms (from alcohol) or long slender needles (from water); v. sol. hot, sl. sol. cold, alcohol, sl. sol. hot water, nearly insol. cold water (Jacobsen a. Schnapauff, *B.* 18, 2841; 19, 1210).

u-**Durene-sulphonic acid** $C_{10}H_{13}(SO_3H)$. Plates or tables containing 2aq. Prepared by dissolving isodurene in ordinary H_2SO_4 at 100°–120°.

Salts.—A'Na: moderately sol. flat prisms. —A'K aq.—A'_2Ba: flat prisms, S. 57 at 15°.—A'_2Ca 3aq.—A'_2Sr 9aq.—A'_2Pb 3aq.—A'_2Co 7½aq. —A'_2Cu.—A'Ag.

Amide [118°] (J.); [143°] (Kelbe a. Pathe, *B.* 19, 1553). Long fine needles, v. sol. alcohol, sl. sol. hot, nearly insol. cold, water (Bielefeldt, *A.* 198, 381; Jacobsen, *B.* 15, 1853).

c-**Durene sulphonic acid** $C_6HMe_4(SO_3H)$ [1:2:3:4:?]. *Prehnitene sulphonic acid.* Formed, together with other products, by the prolonged action of conc. H_2SO_4 upon durene (*q. v.*) or its sulphonic acid. Small needles. Sparingly soluble in moderately dilute H_2SO_4.

Salts.—A'Na aq: small glistening soluble tables.—A'_2Ba: small flat sparingly soluble crystals.

Amide $C_6HMe_4(SO_2NH_2)$: [187°]; small glistening prisms; sol. hot alcohol, sl. sol. cold (Jacobsen, *B.* 19, 1211). The same acid appears to be formed by the sulphonation of the product of the action of MeI and sodium upon bromo-ψ-cumene; the amide of the acid so formed melts, however, at 177° (Kelbe a. Pathe, *B.* 19, 1552).

Durene-di-sulphonic acid $C_6Me_4(SO_3H)_2$. Prepared by dissolving powdered durene in cold fuming sulphuric acid; on pouring the melt into ice and water the sulphonic acid crystallises out. It is much more stable than the mono-sulphonic acid, only being hydrolised when steam is passed through the H_2SO_4 solution, or when the salts are heated to 170° with HCl.

Amide $C_6Me_4(SO_2NH_2)_2$: [above 310°]; small glistening crystals; sl. sol. alcohol (Jacobsen, *B.* 19, 1217).

DURENOL $C_6HMe_4(OH)$. [117°]. (250° i. V.). Formed by fusing sodium durene sulphonate with KOH. Large flat prisms. Sublimable and volatile with steam. Its *bromo- derivative* $C_6BrMe_4(OH)$ forms long glistening prisms, [118°]; its *nitro- derivative* $C_6(NO_2)Me_4(OH)$ yellow crystals, [130°]. By long melting with KOH it is converted into oxy-durylic acid $C_6HMe_3(OH)CO_2H$ [1:3:4:5:6] (Jacobsen a. Schnapauff, *B.* 18, 2843).

Iso-**Durenol** $C_{12}H_{13}.OH$ [108°]. Colourless crystals. Prepared by fusing iso-durene-sulphonic acid with KOH (Jacobsen, *B.* 15, 1854).

c-**Durenol** $C_6H(CH_3)_4(OH)$ [1:2:3:4:5]. *Prehnitol.* [87°]. (266° i. V.). From *c*-durene sulphonic acid by potash-fusion (Töhl, *B.* 21, 904).

Long silky needles (from ligroïn); v. e. sol. alcohol and ether. Not coloured by Fe_2Cl_6. Gives a bromo- derivative [151°].

Acetyl derivative $C_6H(CH_3)_4(OAc)$: [57°]; prisms.

DURIDINE $C_6H(CH_3)_4(NH_2)$. [14°]. (253°). S.G. $\frac{24}{}$ ·978. One of the products obtained by heating xylidine hydrochloride with MeOH (Hofmann, *B.* 17, 1913).—B′HCl (at 100°).—$B'_2H_2PtCl_6$ (at 100°).

Iso-**Duridine** $C_6HMe_4.NH_2$. *Amido-tetra-methyl-benzene.* (250° i. V.) at 740 mm. Formed by heating pseudocumidine or mesidine hydrochloride with methyl alcohol at 200°–300° (Nölting a. Baumann, *B.* 18, 1149). Colourless liquid, which solidifies in a freezing mixture.

Salts.—B′HCl: small white prisms.—$B'_2H_2Cl_2PtCl_4$: yellow tables.

Acetyl derivative $C_6HMe_4.NHAc$: [211°]; white needles, v. sol. alcohol, sl. sol. water.

DUROQUINONE $C_6Me_4O_2$. [111°]. Prepared by reducing di-nitro-durene to durylene diamine with zinc-dust and acetic acid, removing the zinc by H_2S, and oxidising the solution with Fe_2Cl_6. Formed also by the action of warm NaOHAq upon Me.CO.CO.Et (Pechmann, *B.* 21, 1420). Long yellow needles. Sublimable. V. e. sol. ether, chloroform, benzene, alcohol, and acetone, v. sol. hot, but sl. sol. cold, ligroïn. Reduced by zinc and HOAc to a substance [c. 210°], which is easily reoxidised to the quinone (Nef, *B.* 18, 2806; *C. J.* 53, 428; *A.* 237, 5).

DUROYL-BENZOIC ACID *v.* TETRA-METHYL-BENZOYL-BENZOIC ACID.

DURYLIC ACID *v.* ψ-CUMINIC ACID.

Quinone of durylic acid *v.* ψ-CUMOQUINONE CARBOXYLIC ACID.

DURYL METHYL KETONE $CH_3.CO.C_6HMe_4[1:2:3:4:6]$. (254°). From *u*-durene, AcCl, and $AlCl_3$ (Claus a. Forsling, *B.* 20, 3098). Liquid. V. sol. alcohol and ether.

Oxim. [148°]. Small plates.

Phenyl hydrazide [215°]. Needles.

s-**Duryl methyl ketone** $CH_3.CO.C_6HMe_4[1:2:4:5:6]$. [63°]. (251°). From *s*-durene, AcCl, and $AlCl_3$ (C. a. F.). Pearly plates.

Phenyl hydrazide. Small silky crystals; decomposing at 225°.

DI-DURYL SULPHONE $C_6HMe_4.SO_2.C_6HMe_4$. *Sulpho-duride.* [37°]. Formed, together with durene sulphonic acid and its chloride, by the action of sulphuric chlorhydrin (2½ pts.) upon powdered durene at 0°. Long prisms. Can be distilled *in vacuo*. V. sol. alcohol, ether, benzene, and ligroïn, insol. water (Jacobsen a. Schnapauff, *B.* 18, 2841).

DYNAMITE *v.* GLYCERIN.

DYS-ALBUMEN *v.* PROTEÏDS.

DYSLYSIN $C_{24}H_{36}O_3$. [above 140°]. A product of the decomposition of cholic acid obtained either by heating it to 300° or by treating it with dilute HCl or H_2SO_4 (Berzelius, *A.* 33, 139; 43, 1; Theyer a. Schlosser, *A.* 50, 235; Strecker, *A.* 67, 22; Hoppe-Seyler, *J. pr.* 89, 83). Amorphous resin, insol. water, sl. sol. boiling alcohol, sol. ether. Insol. alkalis. Named from its insolubility. Boiling alcoholic KOH reconverts it into cholic acid.

DYSLYTE $C_8H_6N_4O_6$. [189°]. S. ·07 in 97 p.c. alcohol at 10°. Formed, together with eulyte, by treating citraconic acid with conc. HNO_3 (Baup, *A.* 81, 102; Bassett, *Z.* 1871, 701). Long slender needles (from alcohol). Insol. water.

E

EARTHS. The term *earths* is applied to the oxides of a number of the elements which are difficultly reducible to the metallic state. The majority of elements of this class are of very rare occurrence in the concentrated state, being found accumulated in but few minerals, such, for instance, as in *gadolinite*, *cerite*, *keilhauite*, *orthite*, *samarskite*, *euxenite*, and a few other minerals. In minute quantities, however, the earths are disseminated throughout the whole mineral kingdom. Cossa has detected cerium and didymium in all classes of volcanic rocks; certain kinds of clays contain as much as one per cent. of cerium; and didymium may even be detected in sea-water by means of its absorption-spectrum. Yttria, an earth very rarely found in quantity, may be detected in almost every mineral species, in corals, and even in animal bones. Samarium, an element of the earth class, and even more rarely found in quantity than yttrium, seems to have the same ubiquitous character, and is not unfrequently found in appreciable traces in the minerals *celestine*, *strontianite*, and *native carbonate of lead*.

The oxides of the following elements are usually classed together as earths: *barium*, *strontium*, *calcium*, *magnesium*, *beryllium*, *aluminium*, *zirconium*, *titanium*, *thorium*, *lanthanum*, *didymium*, *cerium*, *yttrium*, *erbium*, *terbium*; and the more recently discovered elements, about the existence of some of which there is yet considerable doubt, *scandium*, *ytterbium*, *decipium*, *holmium*, *thulium*, *samarium*, *gadolinium*, and *dysprosium*.

From a chemical point of view some of these elements exhibit characteristics so widely different as to render it necessary to divide them into at least two groups; viz., those whose salts are not ppd. by ammonia, the hydrates being soluble in water and possessing a strongly alkaline reaction; and those ppd. by ammonia. To the first group belong barium, strontium, and calcium, whose oxides are termed the alkaline earths; all the others are ppd. by ammonia.

The analogies shown by the oxides of some of these elements with the oxides of the heavy and easily reducible metals would seem to throw them out of the list of earths; such are magnesium and beryllium; the existence of the stable oxides MgO and BeO seems to indicate that these metals belong to the same group as cadmium and zinc. The same may be said of thorium, zirconium, and titanium, which constitute a natural group with tin, forming the oxides MO_2. As beryllium, thorium, zirconium, and titanium, are almost invariably found associated with the earths proper they are here retained in giving an outline of the chemical methods of effecting the separation of this numerous class of bodies from each other.

It is only within recent years that the list of earths has been so much extended, and there is every reason to believe that the number will be further increased, not so much, it may be, by finding that rare and ill-examined minerals contain new elements, as by discovering that some of the bodies already well known are in reality mixtures of two or more oxides; it is, however, to be remembered that the existence of all the oxides of elements enumerated above is not yet finally proved. The discoveries that have already been made in this field have proved the heterogeneous character of some well-known oxides or earths; this is exemplified below. This splitting up of an earth into two or more constituents is not to be looked upon as an act of *dissociation* (*q. v.*), but is merely the result of more refined methods of attacking the difficult problem of isolating the several already known earths in a state of purity, combined with a very close study of variations in their spectroscopic characteristics when the various elements are isolated from different mineral species. It is sufficient merely to glance over the discoveries that have been made relating to the earths, to understand the difficulties under which this branch of mineral chemistry labours, and upon what facts it is possible to assume, with any degree of certainty, the homogeneous or heterogeneous character of a material. Owing to the great similarity in the chemical reactions of many of the earths, to isolate any particular earth is a most tedious operation, as there are no known sharp methods, such, for instance, as for the separation of silver from copper, or copper from iron. When a pure material has been prepared the further chemical treatment of which fails to produce any variation in the atomic weight of the element, or in the depth of colour of the oxide, or in the intensity of any of the bands in the absorption-spectrum of the salts, it is assumed that the material is of a homogeneous character. But in preparing one particular earth it has been customary to select some mineral in which it predominates, and to purify the earth from all the others that contaminate it in small quantity. Even then only in one or two instances can it be asserted that the oxide is pure; in fact theoretical considerations show that to obtain a pure material by the methods employed is an impossibility. For example, samaria, which is undoubtedly a white oxide, is invariably tinted pale yellow because of a trace of adhering decipia, and the tint may be diminished in depth by numberless repetitions of fractional precipitation; so also yttria is tinted pale yellow by a trace of terbia, although Clève in one instance obtained a small quantity of a pure white colour; gadolina, doubtless a white oxide, has a pale yellow colour due to a trace of decipia; lanthana, a white oxide, can only with great difficulty be obtained free from the last traces of praseodymia which colours it grey, although the absorption-spectrum shows no evidence of its presence. Inversely it may be assumed that those oxides which are coloured are more or less contaminated by the colourless ones, as terbia with yttria, decipia with gadolina and samaria, praseodymia with lanthana, and erbia with ytterbia and scandia. The chemical history of the earths indicates the above method of proceeding to be fallacious, and would seem to show that the only alternative is to isolate the same oxide from a number of different sources, and to examine if there are any differences in the physical characters of the different specimens; such as in the molecular weights, the depth of colour of the oxides, or in the intensity of the bands of the absorption-spectra. The advisability of this method is evident; for it is highly probable that two closely allied elements may exist in one mineral in such quantity as to make it appear to be a homogeneous substance, while the same material isolated from a different source by the same chemical methods may consist of the two oxides in such a totally different ratio as to show its complex character by discrepancies in the molecular weights, colour of the oxides, or the intensity of the bands in the absorption-spectra. This has indeed been found to be the case in several instances; yttria was usually considered to have a pale yellow colour, and this oxide and erbia were the only two oxides which Bunsen and Bahr, as well as Clève, could isolate from *gadolinite*, although Mosander had recorded the existence of a yellow or orange-coloured oxide, associated with these two, which he named terbia. In examining the yttria mineral *samarskite* found in North Carolina, L. Smith and Delafontaine observed that the yttria had a much deeper yellow tint than was usually ascribed to it when extracted from *gadolinite*, and these chemists ultimately succeeded in separating the orange-coloured oxide terbia from the white yttria. More recently De Boisbaudran, examining terbia from different sources, considers himself justified in asserting the existence of a number of oxides having an orange colour, showing no absorption-spectrum, but differing in molecular weights. As another instance: the salts of didymia obtained from *cerite* show a very characteristic absorption-spectrum; Delafontaine, when examining the spectrum of the didymia from *samarskite*, observed that the bands in the blue region of the spectrum differed from those shown by the didymia from *cerite*; and De Boisbaudran, working upon this material from *samarskite*, eliminated the oxide of the element giving the blue bands and gave the element the name samarium. The great preponderance of didymia over samaria in *cerite* had previously masked the existence of the latter, whereas in *samarskite* samaria is relatively abundant compared with didymia, and shows its presence at once by the absorption-spectrum. Marignac again, in examining erbia, discovered that by many repetitions of the process of fractional decomposition of the nitrate by fusion, the pink material yielded a more easily decomposable salt of a white colour, and named the oxide ytterbia; and Nilson, preparing this white oxide ytterbia from erbia, found that the molecular weight differed from Marignac's material. and this he ultimately found to be due to the presence of another white oxide whose nitrate is more readily decomposed by heat than ytterbia; this white oxide Nilson has called scandia. Clève, studying the absorption-spectra of different fractions of erbia, concluded that this oxide is really a mixture of three, the true erbia, and two others which he has called holmia and thulia. Holmia has been examined by De Boisbaudran (*C. R.* 102, 1003) by fractional ppn. of the sulphate by alcohol; it appears to consist of two oxides, holmia, and one which he names dysprosia, both showing absorption-spectra. Finally, the most striking discovery relating to the earths is that made by Von Welsbach (*M.* 5, 508). This chemist has found that by crystallising a mixture of the nitrates of didymium, lanthanum, and ammonium in an acid medium, certain double salts are formed, the fractional crystallisation of which, repeated several hundred times, results in the separation of didymium into two elements, one forming green-coloured salts, hence named *praseodymium*, and the other forming salts of an amethyst colour; this second element Von Welsbach calls *neodymium*; these elements show absorption-spectra of a totally different character. This is a most remarkable discovery when it is considered how much labour Clève and others have given to the preparation of pure didymia and its salts by fractional ppn. without apparently observing any facts to indicate its complex character; and more particularly as one constituent gives green-coloured salts, whereas didymium salts have always been recorded as possessing a red or pink colour (*v.* Didymium, p. 383).

The foregoing facts show how necessary it is to isolate a particular earth from several minerals which contain it in large as well as small quantity, before it can be asserted to be a homogeneous body; and when several specimens have been obtained, the absorption-spectra, the atomic weights of the elements in each, and the depth of tint of the oxides, must agree in all the specimens. Krüss and Nilson (*B.* 20, 2134) have worked upon several minerals, and in particular upon large quantities of *Fergusonite*, and from a study of the absorption-spectra of various solutions they conclude that samarium, erbium, neodymium, praseodymium, and other bodies showing absorption-spectra and considered to be elementary, are in reality of a complex character and consist each of a large number of elements. This result is arrived at judging only by the variations in intensity of the absorption-bands, but it would be premature to attach much weight to the assertions of these chemists until fairly pure specimens of the various bodies have been isolated from the several sources, for it is not improbable that in a mixture of a large number of elements, the absorption-bands of one may influence the intensity of those of another.

The following list of elements comprises the metals of those earths which have as yet been prepared in a fairly pure state, although a few are, as aforesaid, looked upon by some chemists as mixtures of several earths.

Aluminium
Beryllium
Zirconium
Thorium
Scandium
Ytterbium
Yttrium
Erbium
Terbium
Holmium
Dysprosium
Thulium
Decipium
Lanthanum
Neodymium
Praseodymium
Samarium
Cerium
Gadolinium.

Those elements whose salts show absorption-spectra are erbium, holmium, dysprosium, thulium, neodymium, praseodymium, and samarium. The oxides are all white, with the exception of erbia which is pink; holmia and thulia, pink (?); decipia, orange; neodymia, blue (Von Welsbach); praseodymia, dark brown; ceria, pale yellow; gadolina, white (pale yellow, Marignac); terbia, orange.

The chemical methods for effecting the individual separation of the earths are either by fractional fusion of the nitrates, or fractional ppn. with dilute ammonia; those oxides which are ppd. by K_2SO_4 (*v. post*) are all much more basic than those not so ppd., and the order of basicity of the two groups is as follows, beginning with the most basic (assuming the existence of the bodies enumerated as distinct earths):—

$$La > Prd > Nd > Sm > Gd > Dp;$$

and for the yttria group,

$$Y > Tb > ErHoTm > Yb > Sc.$$

An oxide is regarded as more or less basic than another according as it is displaced from its salts with more or less difficulty than the other oxide. The relative basicities of two oxides are determined by fractionally ppg. a solution containing salts of both oxides. Thus if an insufficiency of a pptant. is added to a mixture of two earths in solution in the ratio $\frac{A}{B}$, and the pp. contains the earths in the ratio $\frac{a}{b}$, then A is said to be more or less basic than B according as the ratio $\frac{a}{b}$ is $<$ or $>$ $\frac{A}{B}$; the less basic earth yields more easily to the pptant., the more basic resists its action more.

In the cerite earths, decipia, being the least basic, accumulates in the first pps. and lanthana remains in solution; while in the yttria group, scandia and yttria stand at the two extremes. The oxides ceria, thoria, zirconia, and beryllia, as well as alumina, are easily separated by methods other than fractional ppn. or fusion.

The sources from which the earths are obtained are few. The best known mineral containing these oxides, and apparently the most abundant, is *cerite*, which consists largely of ceria, with about 15 p.c. of lanthana, praseodymia, and neodymia; the amount of samaria and decipia is small, being about three-tenths p.c.; gadolina only a trace; and there is generally a small quantity of the yttria group of earths. *Gadolinite* and *euxenite* are each rich in yttria, erbia, holmia, with a small quantity of ytterbia and scandia; while *samarskite* appears to be the most abundant source of terbia, samaria, and gadolina, together with much yttria.

Separation of the Earths.—Before attempting to isolate the earths individually, they are first separated as completely as possible from the heavy metals and the alkaline earths, and from niobic, tantalic, and titanic acids; fusing the finely ground mineral, should it be a niobate or tantalate, with $KHSO_4$, and digesting with water, will leave Nb_2O_5 and Ta_2O_5 insoluble; if the mineral is a silicate, like *cerite* or *gadolinite*, HClAq or H_2SO_4Aq may be employed to decompose it. The Cu, Bi, &c., in the solution are ppd. by SH_2, and ammonic oxalate is added; if the oxalate is in large excess the filtrate will contain the zirconia as well as beryllia and alumina. The mixed oxalates are well washed, dried, and strongly heated, and the oxides thus formed are dissolved in HClAq; the evolution of Cl indicates the presence of CeO_2; if the heating has been too intense, ZrO_2 and ThO_2 remain insoluble The solution is ppd. by ammonia, and boiled to separate CaO, BaO, and SrO; the pp. is redissolved, ppd. by oxalic acid, and the oxalates are heated. The colour of the strongly heated material will now give some indication of its character. It is invariably of a deep brown or pale yellow colour; the former indicates the presence of much didymia (neodymia and praseodymia), and the latter tint indicates terbia, decipia, or ceria; the colouring materials didymia, terbia, and decipia appear to be peroxides which are reduced and become white, or greenish white, when gently heated in a reducing atmosphere.

The oxides are dissolved in nitric acid; the solution is mixed with three or four times the weight of the oxides of sodic nitrate, evaporated to dryness, and the residue is subjected to gentle fusion to decompose the ceric, thoric, and zirconic nitrates, should these bodies be present; water is added and the liquid is filtered. The spectroscope will now readily reveal the presence of didymia, erbia, and such other earths as show absorption bands; the bands of samaria are very faint and a somewhat conc. solution is required.

The next step in the separation of the earths is to divide them into two groups by ppg. the solution, either as chlorides, nitrates, or sulphates, by K_2SO_4. To the nearly neutral solution more than sufficient K_2SO_4 is added in fine powder to saturate the liquid, which is then allowed to stand some hours with occasional agitation; the pp. that forms is filtered off and washed several times with a saturated solution of K_2SO_4, the operations being done cold. The pp. and solution now contain the following elements:—

Precipitate.

Di, La, Ce, Sm, Dp, Th, Zr, Gd;

Filtrate.

Y, Yb, Er, Ho, Tm, Tb, Sc.

The pp. of Gd-salt is slightly soluble in a saturated solution of K_2SO_4, but for the other elements the separation is practically perfect (*v. post*). Both pp. and filtrate are decomposed with caustic soda, the pps. are well washed till free from sulphates, and both are redissolved separately in HNO_3Aq; if much Ce, Zr, or Th is suspected, the pp. from the solution is again fused with sodic nitrate as before.

The earths Di_2O_3, La_2O_3, &c., are separated from each other by fractional ppn. of their nitrates by cold dilute ammonia: to the dilute neutral solution sufficient ammonia is added to ppt. a considerable portion of the whole, say about nine-tenths; the pp. is filtered off, redissolved in nitric acid, and again ppd. in about the same proportion as before, the operation being repeated upon each pp. till about only one-tenth of the original material remains. All the filtrates are put together, and the operations are repeated as before, and the final small pp. is added to the previous one. The success of this method of operating depends upon the slight differences between the basicities of the various earths, the least basic tending to be ppd. first, and the most basic to remain in solution. The basic powers are, in order of increasing magnitude Dp<Gd<Sm<NdPrd<La; therefore the La_2O_3 tends to accumulate in the filtrates, and the Dp_2O_3, Gd_2O_3 and Sm_2O_3 in the pps. The absorption-spectrum will show that the intensity of the Nd_2O_3 and Prd_2O_3 bands becomes less, and the colour of the oxide obtained by heating the oxalate becomes more nearly white, in the first filtrates as the process is repeated; the least basic material will do the same, inasmuch as Gd_2O_3 and Sm_2O_3 are white and Dp_2O_3 is orange yellow, whereas the intermediate fractions rich in Nd_2O_3 and Prd_2O_3 give very strong absorption-bands, and the strongly heated oxalates are of a deep coffee-brown colour. The difference between the basicity of La_2O_3 and the other earths is much greater than that between any of the other two consecutive earths of the series, as Dp-Gd, Gd-Sm, Sm-NdPrd, so that the purification of La_2O_3 is easy compared with the labour required for the separation of the others. Assuming that the less basic material is obtained free from Nd_2O_3 and Prd_2O_3, as shown by the spectroscope, fractional pptn. is repeated on the material till the filtrates give an oxide of a white colour consisting of Sm_2O_3 and Gd_2O_3, which are separated from each other by taking advantage of the greater solubility of the double sulphate of gadolinium and potassium in a conc. solution of K_2SO_4.

Another method of conducting the separation of the earths consists in using a number of flasks in series, the central one being marked '0,' those to the right marked +1, +2, +3, &c., and those to the left −1, −2, −3, &c. The solution to be fractionated is placed in the central flask marked '0,' and about one-half of the material is ppd.; the pp. is dissolved and placed in −1, and the filtrate is placed in +1. One half of −1 is ppd., the pp. is dissolved and put into −2, and the filtrate into 0; one half of +1 is thrown down, the pp. is dissolved and placed in 0, and the filtrate is put into +2. In this way the operations are repeated till the $+n$ flask contains the most basic earths, and the $-n$ flask the least basic.

The earths not ppd. by K_2SO_4, consisting of Y_2O_3, Er_2O_3, Tb_2O_3, &c., are converted into nitrates and are treated by either of two methods — (1) by fusing the nitrates, or (2) by fractional ppn. with dilute ammonia. The first method would seem to be the more successful, as by its use scandia, ytterbia, holmia, thulia, and erbia have been isolated. The basicities of the earths being in the order Sc<Yb<Er Ho Sm<Tb<Y, the nitrate of scandia tends to decompose at a lower heat and more readily than the ytterbia salt, the latter decomposes before erbia, holmia, &c., and these decompose more readily than yttric nitrate. Hence, if the fusion has been carried nearly to complete decomposition, the fused mass when treated with water will give a solution rich in yttria and terbia, and containing little or no scandia and ytterbia. The insoluble material is redissolved in nitric acid, and again

subjected to fusion as before; the fused mass is treated with water and filtered, the operations being repeated very many times, as in fractional ppn.

The methods given above for separating the earths may be somewhat modified according as one or other of the elements preponderates. In working with the cerite earths the material, as nitrates, is first mixed with sodic nitrate, and subjected to the process of fusion to decompose the very large amount of ceric nitrate present; as the amount of the yttria earths in *cerite* is small, the solution from the insoluble ceric oxide may at once be treated by fractional ppn.; the yttria earths, being very much less basic than La_2O_3 or Di_2O_3, collect completely with the Sm_2O_3 in the first fractions, when this portion is then separated by K_2SO_4. Again, in such minerals as *gadolinite* or *samarskite*, the amount of the cerite earths being small, fractional ppn. or fusion may be at once resorted to with the nitrates, and the most basic portions, containing all the La, Di, Sm, &c., may be finally treated with K_2SO_4.

Several methods of limited application are suitable for the separation of a few of the earths; didymia, containing a trace of lanthana, may be purified by ppn. in a strongly acid solution (HNO_3) with oxalic acid, lanthanic oxalate being much more soluble than the didymic salt; the same process may be employed for separating yttria from terbia, the oxalate of the former being the more soluble; or this separation may be effected by dissolving the oxides in formic acid, and crystallising, the terbic formate being the less soluble. Small quantities of cerium are easily separated by ppg. with large excess of soda, and passing chlorine through the liquid, which leaves the CeO_2 insoluble.

The distinguishing characteristics of the elements scandium, ytterbium, and yttrium are their widely different atomic weights, different spark-spectra, and the slight differences in basicities, these being in the order $Sc<Yb<Y$. Erbia, holmia, and thulia are recognised by the bands in their absorption-spectra; decipia and terbia both give orange-coloured oxides, but differ in the fact that the former is ppd. by K_2SO_4 as a double sulphate, while the latter is not so ppd.; gadolina and samaria, two closely-allied earths, differ also in the solubility of their double sulphates with K_2SO_4 in a conc. solution of this salt, and the former gives no absorption-spectrum.

The earths, known as rare, resemble alumina in being ppd. by ammonia, insoluble in excess, but differ from alumina in being insoluble in excess of soda or potash; they likewise resemble CaO, SrO, and BaO in forming, with the exception of ZrO_2, oxalates which are insoluble in water and oxalic acid or ammonium oxalate, but are slightly soluble in acids; ThO_2 and ZrO_2 are ppd., like Al_2O_3, by sodium thiosulphate. The oxides of the cerite and yttria groups are all assumed to have the formula M_2O_3; most of them form higher oxides by ppg. with ammonia in presence of H_2O_2. Our knowledge of the rare earths is yet very incomplete. J. J. H.

EARTHS, METALS OF THE. The term *earths* is one of those words which perpetuate the connexion of chemistry with alchemy. The meaning given to the term at different periods marks the change from the vague conceptions of the earlier times to the more precise knowledge regarding composition and properties which belongs to modern chemistry. *Earth* was one of the four alchemical essences or elements. In later times the term was applied to all bodies which were insoluble in water and not changed by heat. 'Terra est corpus fossile,' says Boerhave, in his *Elementa Chemiæ* (1732), 'simplex, durum, friabile, in igne fixum, in igne non fluens, in aqua, alcohole, oleo, aëre dissolvi non potens.' As investigation advanced, a separation was made between bodies which had many properties of earths and yet were soluble in water—these were called the alkaline earths—and bodies which were not dissolved by water. Silica, alumina, gypsum, and ferric oxide, were taken to be the typical earths. Lavoisier's demonstration of the change which occurs when a metal is burnt suggested that many earths might be oxides of metals; Davy's discovery of sodium and potassium marked a further step in the acquisition of accurate knowledge of the composition of earths; and the labours of Berzelius and his followers completed the work which the alchemists began.

The earths are the oxides of certain metals; these oxides are all insoluble, or only slightly soluble, in water; the oxides are reduced to metals with difficulty. There is still difference of opinion as to the list of metals whose oxides are to be included in the class of earths, but the matter is not one of great importance. The term is used in the present article only for convenience of classing together a number of elements which show distinct analogies. The metals Al, Ga, In, Sc, Y, La, and Yb resemble each other in so many respects that it is advisable to place them in the same class; thallium also shows distinct analogies with Al, Ga, and In; and the eight elements mentioned more or less resemble the non-metallic element boron.

These nine elements form Group III. in the periodic classification of the elements. This group is divided as follows:—

Group III.

Even series					
2	4	6	8	10	12
B (11)	Sc (44)	Y (89)	La (139)	Yb (173)	—
Odd series					
3	5	7	9	11	
Al (27)	Ga (69·9)	In (114)	—	Tl (204)	

These elements are all metallic except boron; scandium and ytterbium have not been isolated; some of the properties of those metals of this group which have been isolated are presented in the table on the next page.

Chemical properties.—The earth-metals decompose water, some of them at ordinary temperatures, *e.g.* Y and La, others at 100°, *e.g.* Al, and others only at red heat, *e.g.* Tl. They are all oxidised when heated in oxygen, Al and Ga not at all readily; Tl is oxidised even by exposure to air. The metals combine directly with the halogens to form compounds MX_3, and Tl forms also the gasifiable chloride TlCl.

The well-marked oxides of the metals we are considering belong to the form M_2O_3, but Tl also forms the very characteristic oxide Tl_2O; the oxides M_2O_3 are basic, Tl_2O is distinctly alka-

	ALUMINIUM	GALLIUM	YTTRIUM	INDIUM	LANTHANUM	THALLIUM
Atomic weights	27·02	69·9	89·6	113·4	138·5	203·64
	One or more compounds of each element, except Y and La, have been gasified; specific heats have been directly determined, except for Y. Molecular weights unknown.					
Melting points	700°	30°	(?)	176°	(?)	285°
Specific gravities (approx.)	2·6	6·1	(?)	7·3	6·2	11·9
Specific heats	·225	·08	(?)	·057	·047	·034
Occurrence and preparation	Very widely distributed, chiefly as silicate. Obtained by reducing $Al_2Cl_6.2NaCl$ by Na	In very small quantities, as sulphide, in some zinc blendes. Obtained by electrolysing alkaline solution of the sulphate.	With Sc, Yb, La, &c., as silicate in a few rare Swedish minerals. Obtained by reducing $Y_2Cl_6.2NaCl$ by Na, or by electrolysis.	In very small quantities, as sulphide, in some zinc ores. Obtained by reducing oxide by C or H, or ppg. solutions of salts by Zn.	With, Y, Yb, Ce, &c., as silicate in a few rare Swedish minerals. Obtained by reducing La_2Cl_6 by K, or by electrolysing molten $La_2Cl_6.2NaCl$.	In small quantities, chiefly as selenide, fairly widely distributed. Obtained by electrolysis of salts in solution; by ppn. by Al or Zn; or by reducing oxide by KCN or C.
Physical properties	Tin - white, fairly hard, very malleable and ductile, very sonorous.	Silver-white, fairly hard, rather brittle, very low melting-point.	Greyish-powder (little investigated).	White, very soft, lustrous.	White-grey, fairly hard, and ductile.	Very lustrous, malleability and ductility small, very soft.

line, forming the hydroxide TlOH, which is undoubtedly to be classed with the alkalis. The most characteristic salts of the metals of the earths belong to the form M_23X, where $X = SO_4$, SO_3, CO_3, $2NO_3$, $2ClO_3$, $\tfrac{2}{3}PO_4$, &c.; Tl also forms very characteristic salts, Tl_2X, closely resembling those of the alkali metals. The sulphates M_23SO_4 of the odd-series members of the group, except Tl, *i.e.* the sulphates of Al, Ga, and In, combine with alkali sulphates to form alums $M_23SO_4.X_2SO_4.24H_2O$, where M = Al, Ga, or In, and X = alkali metal usually K or NH_4; thallous sulphate Tl_2SO_4 forms an alum in which it takes the place of the alkali sulphate ($Al_23SO_4.Tl_2SO_4.24H_2O$). In the three elements, Al, Ga, In, the tendency to form more than one chloride increases as the atomic weight increases, and also the tendency of the chloride M_2Cl_6 to dissociate into MCl_3 increases as the atomic weight increases. Al, Ga, and Y dissolve in KOHAq with evolution of H; in this respect they show analogies with some of the non-metals. Tl appears to form an oxide TlO_2, and this oxide seems to be acidic. The chlorides $AlCl_3$, $GaCl_3$, and $InCl_3$ exist as gases at very high temperatures; there is evidence of the existence as gases of $GaCl_2$ and $InCl_2$, and possibly of InCl; TlCl has been gasified, but $TlCl_3$ is known only as a solid. These data seem to indicate that the atoms of the earth-metals are trivalent, and perhaps also divalent, in gaseous molecules.

The investigation of the earth-metals is yet very incomplete; so far as facts are available one may say that Al, Ga, and In are very closely related, that Sc, Y, La, and Yb form another family, and that Tl shows relations with the Al family, but is also most distinctly analogous to the alkali metals on one hand and lead on the other hand. Boron, which is the non-metallic member of Group III., has already been considered (*v.* vol. i. p. 524). M. M. P. M.

ECBOLINE *v.* ERGOTININE.

ECGONINE $C_9H_{15}NO_3$ *i.e.* $C_5NH_7Me.CH(OH).CH_2.CO_2H$. ἔκγονος, offshoot. *Tetrahydride of Tetrahydro-β-oxy-methyl-β-pyridyl-propionic acid.* [198°]. Obtained, together with benzoic acid and MeOH, by heating cocaine ($C_5NH_7Me.CH(OBz).CH_2.CO_2Me$) with HCl at 100° (Wöhler, *A.* 121, 372; Lossen, *A.* 133, 351). Boiling baryta, acting on cocaine, forms not only ecgonine but also 'isotropine' $C_8H_{15}NO$ (Calmels a. Gossin, *C. R.* 100, 1143). Monoclinic prisms (containing aq) (from alcohol); $a:b:c = {\cdot}8136:1:{\cdot}6277$; $\beta = 87° 8'$. V. sl. sol. water, m. sol. alcohol, insol. ether.

Reactions.—1. The product obtained by heating with MeI gives, after warming with silver chloride and Ag, a methylo-chloride, whence $(C_9H_{15}NO_3MeCl)_2PtCl_4$ may be obtained (Gintl a. Storch, *M.* 8, 78).—2. Oxidation with $KMnO_4$ gives succinic acid (Einhorn, *B.* 21, 50).—3. Heating with H_2SO_4 forms an anhydride (?), whose barium salt $C_{18}H_{26}BaN_2O_5$ is crystalline (Calmels

a. Gossin, *C. R.* 100, 1143).—4. Distillation with BaO gives methylamine.

Salts.—$B'_2H_2PtCl_6$: [226°]; yellow powder, extremely sol. water, sl. sol. alcohol. When its solution is heated there is formed B'_2PtCl_4 as yellowish needles, v. sol. water, nearly insol. alcohol (C. a. G.).—B'HCl. [246°]. Sl. sol. alcohol (Liebermann, *B.* 21, 2351).

Benzoyl derivative $C_9H_{14}O_3NBz$. [189°]. (M.); [192°] (S.); [195°] (L. a. G.). Formed as a by-product in the preparation of cocaine (Merck, *B.* 18, 1594). Formed also by boiling cocaine with water for several hours (Einhorn, *B.* 21, 47). Also from ecgonine and Bz_2O (Liebermann a. Giesel, *B.* 21, 3196). Flat colourless prisms; sol. water and alcohol, nearly insol. ether. Crystallises also in prisms containing 4aq [92°] and [140°]. Decomposed by HCl into benzoic acid and ecgonine. Partially converted by MeI, dissolved in MeOH in presence of alkali into cocaine, although the greater part is simply resolved into benzoic acid and ecgonine (Skraup, *M.* 6, 556; *cf.* Merck, *B.* 18, 2264). In the same way, by heating benzoyl-ecgonine with alkyl iodides, the following homologues of cocaine may be prepared, ethyl-benzoyl-ecgonine $C_{16}H_{18}EtNO_4$: [108°]; monoclinic prisms; propyl-benzoyl-ecgonine $C_{16}H_{18}PrNO_4$ [79°]; and isobutyl-benzoyl-ecgonine $C_{16}H_{18}(CH_2Pr)NO_4$ [62°] (Novy, *Ph.* [3] 18, 233). According to Einhorn (*B.* 21, 3443) the first of these homologues of cocaine is a liquid and the second a solid [58°].

Salt of Benzoyl-ecgonine $B'HAuCl_4$: sparingly soluble golden leaflets.

Anhydro-ecgonine $C_9H_{13}NO_2$ *i.e.* $C_5NH_7Me.CH:CH.CO_2H$ [235°]. Formed by the action of PCl_5 (Merck, *B.* 19, 3002) or $POCl_3$ (Einhorn, *B.* 20, 1221) on ecgonine. Crystals, v. sol. water and alcohol, almost insol. other solvents. With Br it forms $C_9H_{13}Br_2NO_2$, whose hydrochloride $C_9H_{13}Br_2NO_2HCl$ melts at 184°. It forms a perbromide [156°].

Salts.—B'HCl. [241°].—$B'_2H_2PtCl_6$. [223°].—$B'HAuCl_4$.—$B'HI_3$ [186°].—B'HBr [155°].

Ethyl derivative $C_9H_{12}EtNO_2$. Oil. Forms a hydrochloride [244°].—$B'H_2PtCl_6$ [211°].

ECHICERIN *v.* Dita Bark.

ECHITIN *v.* Dita Bark.

ECHITENINE *v.* Dita Bark.

EFFLORESCENCE. The formation of a loose powdery deposit on the surface of a solid body is termed *efflorescence.* Some hydrated salts lose water of crystallisation by exposure to the air, and the surface becomes covered with a deposit of the dehydrated salt; crystals of $Na_2CO_3.10H_2O$, for instance, effloresce in this way, the surface becoming $Na_2CO_3.5H_2O$. If a porous body is filled with a salt solution, the solution will be drawn by capillary action to the surface of the solid, and if the body in solution crystallises on the surface of the solid the phenomenon is called efflorescence; thus, the formation of nitre on the surface of the soil, or of sodium carbonate on walls, is an example of efflorescence. The term is also applied to the creeping of a solution up the sides of a vessel and deposition of the dissolved body; thus, if a solution of salammoniac is exposed to the air, crystals are formed where the surface of the liquid touches the sides of the vessel; the liquid then rises, by capillary action, between these crystals, and more crystals are formed above the first layer, and so on.

M. M. P. M

EGG ALBUMEN *v.* Proteïds.

EICOSANE *v.* Icosane.

ELÆOMARGARIC ACID $C_{17}H_{30}O_2$. [48°]. Occurs as glyceride in the oil from the seeds of *Elæococca Vernicia* (Cloëz, *C. R.* 81, 469; 82, 501; 83, 943). Trimetric tables v. e. sol. ether. Absorbs oxygen from the air, becoming resinous. Sunlight converts the oil of Elæococca into a solid fat, which on saponification gives elæostearic acid [72°].

ELÆOPTENE. The portion of a natural essential oil that does not readily solidify.

ELAIDIC ACID. The solid polymeride obtained by the action of nitrous acid on Oleïc acid (*q. v.*).

ELAIDIN. The solid polymeride of Oleïn, *v.* Oleïc acid.

ELASTIN *v.* Proteïds, *Appendix C.*

ELATERIN $C_{20}H_{28}O_5$. Occurs in the spurting cucumber (*Momordica Elaterium*) (Zwenger, *A.* 43, 359; Morrus, *A.* 2, 366; Power, *Ph.* [3] 5, 645). Hexagonal tables, insol. water, sl. sol. ether, v. sol. alcohol. Purgative. Gives a carmine colour with phenol and H_2SO_4 (Lindo, *Fr.* 17, 500; *cf.* Johannson, *Fr.* 24, 156).

ELECTROLYSIS. The separation of a compound into parts effected by the passage of an electric current. A compound which is decomposed by the passage through it of an electric current is called an *electrolyte*; the parts into which it is separated are called the *ions.* When different electrolytes are decomposed by a current, the masses of the ions which carry with them equal quantities of electricity are in the proportion of the chemical equivalents of these ions. Conversely the masses of several ions which are chemically equivalent produce equal quantities of electricity by their combination with other ions; thus, suppose 32·7 grams of zinc were dissolved in sulphuric acid, 28 grams of iron in hydrochloric acid, and 9 grams of aluminium in potash, the quantity of electricity set in motion by each action would be the same. The electricity behaves as if it were divided into atoms, one of which is attached to each monovalent ion, two to each divalent ion, and so on.

In some cases electrolysis proceeds as if the mass of the electrolyte expressed by its chemical formula were being separated into ions; in other cases the action proceeds as if the mass of electrolyte decomposed by the current were a multiple of that expressed by the formula. There are some binary compounds which are not electrolytes, but which undergo electrolysis when mixed with other compounds that also are not themselves electrolytes. The application of the facts of electrolysis to chemical processes will be dealt with in the art. Physical methods.

M. M. P. M.

ELECTRONEGATIVE and **ELECTROPOSITIVE.** When a binary salt is electrolysed into its elements, one of the elements separates at the negative electrode and the other at the positive electrode; the former element is said to be electropositive towards the latter. An element may be electropositive towards another element and at the same time electronegative towards a third element; thus in the electrolysis of a metallic sulphide the sulphur will separate at the positive electrode, but in the electrolysis of sulphur chloride the sulphur separates at the negative electrode; sulphur is negative towards metals but positive towards chlorine. The terms electropositive and negative are used in chemistry as practically synonymous with the terms basylous and chlorous. The classification of elements into positive and negative is of use, inasmuch as with this property a number of others are associated; thus, if we know that an element is positive to many others we conclude that its chemical properties are those characteristic of metals; if, on the other hand, the element is negative to a number of metals, we conclude that its oxides will be acidic, that it will not form salts by replacing the hydrogen of acids, that it will possibly form a hydride, and that generally it will be characterised by non-metallic properties. M. M. P. M.

ELEMENTS. Although the notion of an element or elementary body is one of the remotest antiquity, it has reached its present form by a process of slow growth. The Aristotelian elements—earth, water, air, and fire—represented properties or conditions rather than actual substances; and the same may be said of the alchemical elements—salt, sulphur, and mercury. A very casual review of the older chemical writings will show that these conceptions were scholastic rather than scientific, and yet they served their purpose in a primitive way and aided to some extent in the classification of material things. In a strictly chemical sense, the modern idea of an element, together with its implied distinction between elementary and compound bodies, seems to have originated with Boyle, who, in his *Sceptical Chymist* and other essays, vigorously combated the earlier notions. He taught that such substances were to be regarded as elementary as were not capable of further separation, and which, being obtainable from compounds, could yield like compounds again. Such elements, however, he did not specifically define, nor did he assign any positive limit to their number.

From this point the conception of chemical elements slowly developed, changing as the resources of analysis changed, becoming more definite with the introduction of quantitative methods into chemistry, until with the decomposition of the alkalis and alkaline earths by Davy, and the discovery of the true nature of chlorine, it crystallised into its present form. To-day the myriads of known substances are all capable of ultimate analysis, and they are reduced at last to about sixty-nine or seventy simple bodies, which resist all efforts of the analyst to decompose them further. These simple bodies, or *elements*, are as follows:—

Aluminium
Antimony
Arsenic
Barium
Beryllium
Bismuth
Boron
Bromine
Cadmium
Cæsium
Calcium
Carbon
Cerium
Chlorine
Chromium
Cobalt
Copper
Didymium
Erbium
Fluorine
Gallium
Germanium
Gold
Hydrogen
Indium
Iodine
Iridium
Iron
Lanthanum
Lead
Lithium
Magnesium
Manganese
Mercury
Molybdenum
Nickel
Niobium
Nitrogen
Osmium
Oxygen
Palladium
Phosphorus
Platinum
Potassium
Rhodium
Rubidium
Ruthenium
Samarium
Scandium
Selenion
Silicon
Silver
Sodium
Strontium
Sulphur
Tantalum
Tellurium
Terbium
Thallium
Thorium
Tin
Titanium
Tungsten
Uranium
Vanadium
Ytterbium
Yttrium
Zinc
Zirconium

To these may perhaps be added a few which are still doubtful, such as norwegium, holmium, thulium, &c., and some which are but dimly recognised as present in the cerite and gadolinite earths. It is also probable that some of those in the list are really not elementary substances, *e.g.* didymium.

Upon comparison, these elements are found to fall into well-marked natural groups, the members of each group showing close kinship, both as regards themselves and their compounds. At first the classification of the elements was superficial and tentative, being based upon partial resemblances; and even the broad division of them into metals and non-metals was far from being satisfactory. To the earlier chemists nitrogen and bismuth had nothing in common, carbon and tin were totally unlike, while vanadium and chromium were classed together, and so too were tellurium and antimony. But by means of the hypothesis of valency a clearer insight was gained into the true relationships of the elements, and in the announcement of the periodic law (*q.v.*) by Newland, Mendelejeff, and Lothar Meyer, their orderly sequence was at last definitely perceived. To-day all classification of the elements is based primarily upon that law, and illustrates chemical function rather than external properties. The former is fundamental, the latter are but secondary. Furthermore, in consequence of the periodic law all the physical characteristics of the elements are now thought to depend ultimately upon atomic mass, and thus their classification is directly correlated with the atomic theory.

Omitting a very few of the rarer and more imperfectly known elements, the following elementary groups may be distinctly recognised. For the connexion of the several groups with each other the article on the periodic law should be consulted (*cf.* also CLASSIFICATION, p. 203). By suitable divisions the existence of sub-groups is indicated:—

1	2	3	4	5	6	7	8
H	Be	B	C	N	O	F	Fe
—	—	—	Si	P	S	Cl	Ni
Li	Ca	Al	Ti	V	Se	Br	Co
Na	Sr	Ga	Ge	As	Te	I	—
K	Ba	In	Zr	Sb	—	—	Cu
Rb	—	—	Sn	Bi	Cr	Mn	Ag
Cs	Mg	Sc	Pb	—	Mo		Au
	Zn	Y	—	Nb	W		—
	Cd	La	Ce	Ta	U		Rh
	Hg	Yb	Th	—			Ru
		—		Di			Pd
		Tl		Er			Ir
							Os
							Pt

In each of these groups, or, more precisely, in each of the sub-groups, if the elements are arranged in the order of their atomic weights, there is a regular gradation of properties from the lowest to the highest. Among their compounds precisely similar regularities appear, and exceptions are quite uncommon. If one element in a group forms certain well-defined compounds, we may fairly expect them to be paralleled by every other element in the same series, and their points of dissimilarity will follow a regular serial order. Throughout each group, with a few exceptions, there seems to be one dominant valency representing the maximum stability among the derivatives of the members of the group, and these derivatives are frequently isomorphous. Indeed isomorphism between analogously constituted compounds is good evidence of chemical kinship, although it is not proof positive.

As regards abundance, association in nature, and modes of occurrence, the elements differ widely. Including the atmosphere and the ocean, the mass of the earth's crust is mainly made up of thirteen of them, namely, oxygen, hydrogen, nitrogen, carbon, chlorine, sulphur, aluminium, calcium, magnesium, iron, potassium, sodium, and silicon. Certain others, such as fluorine, manganese, lead, and phosphorus, are relatively common, and others, like gallium, indium, and germanium, are exceedingly rare. Comparatively few of the elements are found free in nature, and these are oxygen, hydrogen, nitrogen, carbon, sulphur, tellurium, arsenic, antimony, bismuth, copper, silver, gold, mercury, zinc, tin, lead, iron, and the six platinum metals. Of these only nitrogen, gold, and the platinum group appear to be more abundant free than in a state of union. Compounds are the rule, native elements the exception. In general terms, like elements occur under like conditions, and often in association with each other. Thus cobalt and nickel are seldom found entirely apart, the rarer earths are almost always commingled, and the platinum metals always occur more or less together. Apart from the commoner rock-forming elements, the so-called 'heavy metals' are chiefly found segregated in veins which are produced by infiltration; while the cerium and yttrium groups, beryllium, zirconium, thorium, &c., exist almost solely in granitic intrusions. In sedimentary or detrital rocks the rarer elements which perhaps were present in the parent formations are so widely scattered as to be no longer discernible. The older rock masses yield by far the larger proportion of the known elements. Even in volcanic outflows the number of elements present seems to be relatively small, perhaps because no segregating influence has rendered the presence of the scarcer substances distinctly manifest. In organic matter the elements carbon, hydrogen, oxygen, nitrogen, sulphur, and phosphorus are the dominating constituents.

In the beginnings of chemistry the fact that one substance could be transformed into other substances gave rise to all manner of alchemical speculations. Transmutations of matter gave the young science its only *raison d'être*, and no good reason existed for assigning any limit to such transmutability. The labours of the alchemists, therefore, were not at all unphilosophical, but on the contrary they represented efforts at generalisation which were perfectly legitimate in their day. But as the modern conception of an element developed, limitations not previously recognised became evident, and the pendulum of chemical opinion swung over towards a belief in the absolute independence and individual integrity of the elementary bodies. From this point of view all theorising as to the nature of the elements became unprofitable, and, indeed, was put outside the proper range of scientific investigation.

Of late years, however, the question has been reopened, the ultimate character of the elements is no longer positively assumed, and the belief is gaining ground that they have been derived from still simpler forms, possibly one form, of matter by some process of evolution. It will be observed that the only evidence in favour of their elementary nature lies in our present inability to decompose them, and that evidence is purely negative. It signifies merely a limitation in our immediate resources; not a limitation essential to the things themselves. On the other hand, the elements are connected by so many intimate relations that their complete independence of each other is hardly supposable. These relations, being definite and surely not accidental, need some hypothesis to explain them, and such an hypothesis, if not fully framed as yet, is at least progressing in its formative stages. The chief lines of discussion now open are as follows:

First, on the basis of the periodic law (*v.* CLASSIFICATION and PERIODIC LAW). In his memorable paper upon that subject Mendelejeff arranged the elements in a tabular scheme, in which certain gaps existed. These gaps, he claimed, should be filled by undiscovered elements, for three of which he predicted the properties in considerable detail. Several years later, in 1876, Lecoq de Boisbaudran discovered gallium, and that metal was found to fill one of the gaps perfectly, conforming with curious accuracy to Mendelejeff's predictions. Since then scandium has been discovered by Nilson, and germanium by Winkler, and they with striking definiteness confirm the remainder of the prophecy. In brief, the prediction of these three metals and its subsequent confirmation would not have been possible were the elements entirely distinct and unrelated. Again, if we plot graphically any set of physical properties of the elements, using them for abscissæ and the atomic weights for ordinates, the periodic relations become strikingly manifest. This is seen in the case of Lothar Meyer's curve of atomic volumes, in which similar elements occupy similar places, and by means of which volumes not actually measured can be approximately estimated. Although as yet no such curve has been interpreted mathematically, there is little doubt but that in time the relations which are so expressed will receive accurate formulation.

Secondly, there is spectroscopic evidence in favour of elementary evolution. If we accept the nebular hypothesis as to the origin of the solar system, we must give weight to the varying chemical complexity of the heavenly bodies. First, the nebulæ themselves are gaseous, and consist very largely of hydrogen. In the whiter, and presumably hotter, stars a few other substances appear, more are found in the sun, and finally we have the cooled planet, seemingly the most complex of all. This evidence was first summed up by Clarke in 1873 (*Popular Science Monthly*, January 1873), who drew from it the conclusion that the evolution of planets from nebulæ had been accompanied by an evolution of the chemical elements. In November of the same year, in a letter to Dumas, Lockyer put forth a similar conception, resting on the same evidence, and argued that in the hotter stars the elements are dissociated. This hypothesis has since been somewhat amplified by Lockyer in numerous publications, and has attained considerable notoriety. It may be further emphasised by the fact that the thirteen commonest elements are all of relatively low atomic weight, while the higher, denser, and probably more complex metals are, as a rule, scarce. Of course the weight of the latter argument is weakened by our ignorance of the earth's interior, and the fact that the mean density of our planet is much greater than that of its crust. The heavier elements may be relatively more abundant near the centre of the earth, as the lighter ones are at the surface.

Still a third line of argument has been fruitful in speculative literature, namely, the study of relations between the atomic weights. In 1829 Doebereiner showed that certain elements constituted triads, in which the middle term had an atomic weight nearly the mean of the atomic weights of the extremes. Such a triad is formed by calcium, strontium, and barium, by chlorine, bromine, and iodine, and by lithium, sodium, and potassium. In 1851 this matter was discussed independently by Pettenkofer and by Dumas, and since then many other writers have studied it. It is now, of course, supplanted by the more general periodic law; but it led to one conception of curious interest. It was early noticed that each triad had certain resemblances to the series formed by organic radicles, as in the paraffin and olefine groups, and the question was raised whether a real analogy might not exist. Now in any organic series isomerism among the derivatives increases as we ascend, and a similar rule seems to hold in some groups of elements. One example will suffice. The metallic chlorides and bromides rarely, if ever, assume allotropic or *isomeric* conditions. But among the iodides, allotropy seems to be common; illustrations are furnished by the iodides of antimony, mercury, and cadmium. Each of these salts exists in at least two distinct modifications, while the corresponding chlorides and bromides show no similar variability. In itself this argument carries little weight, but with other evidence it adds to the strength of the modern position.

Passing over all other discussions concerning relations between the atomic weights, we now come to one controversy which still has living interest; the controversy over 'Prout's law.' In 1815 Prout suggested that hydrogen, the lightest of the elements, might be the one primal form of matter, and claimed that the atomic weights of all the other elements were whole multiples of that of hydrogen. This hypothesis as to the atomic weights broke down in its original form, but in 1859 Dumas endeavoured to show that it held as regards half and even quarter multiples. Then came Stas, with his marvellous determinations of many equivalent ratios, which seemingly proved the absolute untenability of Prout's law, even with Dumas' modifications. In consequence of Stas' researches, Prout's law has been of late years out of favour among chemists, and it has generally been assumed that the question was settled adversely. But in 1880 Mallet published his paper upon the atomic weight of aluminium (*T.* 1880. 1003). In this paper he cites the atomic weights of eighteen elements which he regards as fairly well determined, and shows that ten of them have values varying less than 0·1 from even multiples of unity. This concordance may be accidental; but under the theory of probabilities the chances are 1097·8 to 1 against mere coincidence. Two years later, Clarke, in his 'Recalculation of the Atomic Weights,' extended Mallet's argument to sixty-six elements, of which forty had atomic weights, as then determined, falling within the limit of 0·1 variation from theory.[1] The forty agreements include nearly all the trustworthy determinations, while the twenty-six exceptions are mostly among elements of which the atomic weights had been defectively ascertained. This evidence strengthens materially the argument used by Mallet. It must be remembered that the methods ordinarily employed for computing atomic weights tend to develop apparent variations, through the multiplication of seemingly insignificant errors. The conclusion to be drawn from the whole discussion is, that some law like Prout's, if not identical with Prout's, actually exists; for so large a proportion of close coincidences could hardly be due to mere chance. In this connexion the observation of Meyer and Seubert (*C. J.* 47, 430), that about one-fourth of the elements have atomic weights approximating nearly to even multiples of one-half the atomic weight of oxygen, is surely worth noting. Recently there have been several attempts to bring the atomic weights under one general mathematical law, but the work so far done is hardly complete enough to warrant farther notice. The most promising effort is probably that of G. Johnstone Stoney (*Pr.* 44, 115). The whole question, however, is conditioned by discussions upon the possible variability of the atomic weights and the constancy of chemical composition, such as have been raised by Schützenberger (*Bl.* 39, 258), Butlerow (*ibid.* p. 263), and Cooke (*Am.* [3] 26, 310). Little weight is at present attached to that class of speculations, although the arguments which they involve cannot wholly be ignored.

To a certain extent the nature of the elements is considered by Sir Benjamin Brodie in his 'Ideal Chemistry' and his 'Calculus of Chemical Operations;' but along lines of reasoning which cannot well be entered upon here. Very recently also the subject has been extensively treated by Crookes, and from a novel point of view. He has studied the phosphorescent spectra of the rare earths; and has found that by working with products which represent hundreds of fractional precipitations, he can get strikingly different spectra for what is to all chemical tests one and the same oxide. Thus yttria, after many fractionations, divides into products which are unlike spectroscopically; just as if the molecules of the original earth had either been sorted out from a mixture, or else split up into new groups. These products, differing from ordinary yttria, are the oxides of what Crookes provisionally calls 'meta-elements.' In the same category, perhaps, we must place the neodymium and praseodymium of Auer von Welsbach, derived from didymium; and also the many doubtful earths obtained from samarskite, gadolinite, &c., by Marignac, De Boisbaudran, and Krüss and Nilson. Unfortunately we do not yet know how to interpret all the phenomena, and the evidence admits of various explanations. We may have merely allotropes to deal with, or there may have been a veritable splitting up of relatively unstable elements. That the actual number of distinct earthy oxides should be very largely increased is unlikely, for they fit no vacant places in the periodic system. Crookes himself interprets the evidence thus:—Following along the line of elementary evolution, he conceives that matter, as it developed from the original 'protyle,' passed from stable point to stable point through intervals of instability. Around each accretion of the primitive stuff into a definite element there may be gathered a few particles of intermediate material; and these 'by-products' of elementary manufacture, separable only by long fractionations, may give rise to the phenomena observed in the spectra of yttria. The main line of evolution he represents by a lemniscate curve.

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[1] When O = 16 as the base of the system.

This work of Crookes, as represented in his address of 1886 before the British Association, and in two later lectures before the Chemical Society (*C. J.* 53, 487), brings us face to face with the final question of all. Admitting that the elements have been somehow evolved from simpler primal forms, can the process ever be repeated or reversed artificially? To this question no answer is now possible; but it seems likely that if a transmutation of so-called elementary matter should ever be effected in the laboratory, it will be by the very slow development, under conditions of prolonged chemical stress, of change in traces only.

F. W. C.

ELEMI. A name given to various resins. *Elemi occidentale* is said to be the produce of *Icica Icicariba*; *Elemi orientale* to come from *Amyris ceylonica*. *Elemi ægyptiacum* is perhaps produced by *Elæagnus hortensis*. Translucent resins, used in making varnishes. Some specimens contain amyrin (*q. v.*) and elemin. Elemin forms thin six-sided prisms [200°] (Johnston, *A.* 44, 338; Rose, *A.* 32, 297; 40, 307; Hess, *A.* 29, 139; Baup, *J. Ph.* [3] 20, 321; Buri, *N. Rep. Pharm.* 25, 193). Arbol-a-brea resin contains bryoïdin $C_{20}H_{38}O_3$ [136°] (Flückiger, *J.* 1875, 860). According to Stenhouse and Groves (*A.* 180, 253) incense-resin (from *Icica heptaphylla*) contains conimene $C_{15}H_{24}$ and icacin $C_{46}H_{76}O$. When elemi resin derived from *Amyris elemifera* and *A. ceylonica* is distilled with zinc-dust it yields toluene, *m*- and *p*-ethyl-toluene, and ethyl-naphthalene (Ciamician, *G.* 9, 310; *B.* 11, 1344).

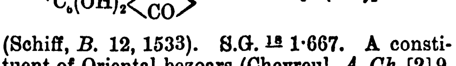
Oil of elemi $C_{10}H_{16}$. (166°) (Stenhouse, *A.* 35, 304); (174°) (Deville, *A.* 71, 352). S.G. ^{24} ·852. V.D. 4·0. $[\alpha_D] = -90°$. Oil, obtained by distilling elemi with steam. HCl forms solid inactive $C_{10}H_{17}Cl$ and a liquid isomeride.

ELEMIC ACID $C_{35}H_{56}O_4$. [215°]. $\alpha_D = -3·5°$. Occurs in elemi, and purified by means of the K salt (Buri, *Ph.* [3] 8, 601).

Properties.—Large crystals (from alcohol). Insol. water, sol. alcohol and ether, sl. sol. CS_2. Its alcoholic solution reddens litmus.

Salt.—KA'18aq : needles.

ELLAGIC ACID $C_{14}H_6O_8$ *i.e.*



$$CO\left\langle\begin{matrix}C_6H(OH)_3\\ |\\ C_6(OH)_2\left\langle\begin{matrix}O\\CO\end{matrix}\right\rangle\end{matrix}\right. \quad \text{or} \quad \left\langle\begin{matrix}C_6H(OH)_2.CO.O\\C_6H(OH)_2.CO.O\end{matrix}\right\rangle$$

(Schiff, *B.* 12, 1533). S.G. ^{18} 1·667. A constituent of Oriental bezoars (Chevreul, *A. Ch.* [2] 9, 629; Braconnot, *A. Ch.* [2] 9, 187; Pelouze, *A. Ch.* [2] 54, 367; Taylor, *P. M.* [3] 24, 354; Wöhler a. Merklein, *A.* 55, 129). Occurs also in sprouts of the divi-divi (Löwe, *Fr.* 14, 40; Barth a. Goldschmiedt, *B.* 11, 846; 12, 1239; Cobenzl, *M.* 1, 671) and in oak bark (Etti, *M.* 1, 266) and fir bark (Strohmer, *M.* 2, 539).

Formation.—1. From gallic acid or tannin, by treatment with iodine, $POCl_3$, PCl_5, or As_2O_5 (Griessmayer, *A.* 160, 55; Löwe, *Z.* 1868, 603). It is also deposited as a grey powder when a decoction of gallnuts is left exposed to the air.—2. By heating gallic ether with aqueous NaOH at 60° (Schiff, *B.* 12, 1533).

Preparation.—Bezoars are dissolved in strong aqueous KOH in the cold; CO_2 is then passed in, when potassium ellagate is ppd. This is recrystallised from water, and the acid is liberated by hydrochloric acid.

Properties.—Minute yellowish prisms (containing 2aq). Insol. water and ether, sl. sol. alcohol. A solution in conc. KOHAq when exposed to the air deposits black crystals of 'potassium glaucomelanate' $C_{12}H_4K_2O_7$ (?), which is reconverted into ellagate by boiling water. Conc. H_2SO_4 dissolves ellagic acid without change. Fe_2Cl_6 gives a greenish colour becoming black.

Reactions.—1. Distillation with *zinc-dust* gives fluorene $C_{13}H_{10}$.—2. *Sodium amalgam* in alkaline solution gives 'glauco-hydro-ellagic acid' $C_{14}H_{10}O_7$, 'rufo-hydro-ellagic acid' $C_{14}H_{10}O_6$ (Rembold, *B.* 8, 1494; Cobenzl, *M.* 1, 671), an acid $C_{14}H_{10}O_9$, and finally (γ)-hexa-oxy-diphenyl. 3. *Potash-fusion* gives (β)-hexa-oxy-diphenyl (B. a. G.).—4. Boiling conc. KOHAq gives hexa-oxy-diphenylene ketone.

Salts.—K_2A'' (at 150°) : minute prisms.—$K_2A''KOH$ (?) : grey powder.—$Na_2A''aq$: pale yellow crystalline powder, sl. sol. water.—$NaHA''aq$ (at 100°).—$Ba_3H_3A''_2$ (at 140°) : lemon-yellow insoluble pp.—$PbA''aq$: amorphous yellow pp.; becomes olive-green on drying.

Tetra-acetyl derivative $C_{14}H_2Ac_4O_8$. Yellow crystalline powder, sl. sol. water.

ELLAGITANNIC ACID $C_{14}H_{10}O_{10}$. Occurs in divi-divi and myrobalanes (Löwe, *Fr.* 14, 44). Amorphous brownish mass. Water at 110° converts it into ellagic acid.—$(C_{14}H_{10}O_{10})_2 5PbO$.

ELUTRIATION. The separation of lighter from heavier particles by washing.

EMETINE $C_{30}H_{40}N_2O_5$ (?). [65°-74°]. S. ·1 in the cold. Occurs in ipecacuanha root (Pelletier a. Magendie, *A. Ch.* [2] 4, 172; Buchner, *Repert. Pharm.* 7, 289; Dumas a. Pelletier, *A.*

Ch. [2] 24, 180; Lefort, *J. Ph.* [4] 9, 241; Pander, *C. C.* 1872, 440; Glenard, *C. R.* 81, 100; Lefort a. F. Wurtz, *C. R.* 84, 1299; Power, *Ph.* [3] 8, 844; Kunz, *Ar. Ph.* [3] 25, 461; Podwyssotzky, *Ph.* [3] 10, 642); Kremel, *Ar. Ph.* [3] 26, 419).

Preparation.—Ipecacuanha is exhausted with ether and ligroïn and the residue extracted with (85 p.c.) alcohol; the extract is evaporated to a syrup, and Fe_2Cl_6 added to ppt. tannin; excess of Na_2CO_3 is added, and the emetine extracted with hot ligroïn.

Properties.—Needles (from ligroïn). Sl. sol. water, v. sol. chloroform, EtOAc, alcohol, CS_2, and essential oils, sl. sol. ligroïn, ether, and benzene. Alkaline reaction. Coloured yellow by sunlight. Produces vomiting. Except the tannate, all its salts are amorphous. Sulphomolybdic acid gives a brown colour, changed by HCl to indigo blue. Potassium-bismuth iodide gives a pp., as do other re-agents for alkaloids.

Salts.—$B'H_2PtCl_6$: yellowish-white powder. —$B'H_2Cr_2O_7$.—B'MeI.—B'MeOH.

EMODIN *v.* TRI-OXY-METHYL-ANTHRAQUINONE.

EMULSIN. A neutral substance contained in sweet and in bitter almonds, and possessing the power of acting as a ferment on the amygdalin of the latter in presence of water, converting it into benzoic aldehyde, HCy, and glucose (Robiquet, *J. Ph.* 24, 326; Thomson a. Richardson, *A.* 29, 180; Ortloff, *Ar. Ph.* 48, 16; Bull, *A.* 69, 145; Johannsen, *Bied. Cent.* 1888, 326). It may be obtained by leaving an aqueous extract of almond cake at 23° for a few days, filtering, and ppg. with alcohol. White amorphous mass, sol. water. The hydrolytic power of emulsin is destroyed by boiling.

ENCEPHALIN *v.* CEREBRIN.

n-**ENNANE** C_9H_{20}. *Nonane.* Mol. w. 128. [-51°]. (150°). S.G. $\frac{0}{4}$ ·733; $\frac{100}{4}$ ·6541. From pelargonic acid $C_9H_{18}O_2$ by distillation with P and HI (Krafft, *B.* 15, 1692).

Ennane C_9H_{20}. (148°). S.G. ^{21} ·7124. V.D. 65·4 (for 64). Occurs in Galician petroleum (Lachowicz, *A.* 220, 194).

Ennane C_9H_{20}. (136°). S.G. $\frac{12}{4}$ ·742. V.D. 4·59 at 180°. Occurs in petroleum (Lemoine, *Bl.* [2] 41, 163).

Ennane C_9H_{20}. (130°). S.G. ^{0} ·743. V.D. 4·47 at 190°. Occurs in petroleum (L.).

Ennane C_9H_{20} *i.e.* $Pr.CH_2.CH_2.CH_2.Pr$. (132°). S.G. ^{0} ·725. From isoamyl iodide, isobutyl iodide and Na (Wurtz, *A. Ch* 3] 44, 275).

Ennane C_9H_{20}. (130°). From isopropyl iodide and Na (Silva, *B.* 5, 984).

ENNDECANE $C_{19}H_{40}$ *i.e.* $CH_3(CH_2)_{17}CH_3$. *Nonadecane.* [32°]. (330°). S.G. $\frac{32}{4}$ ·7774; $\frac{99}{4}$ ·7823. From $C_{19}H_{38}Cl_2$ by heating with HI and phosphorus. Occurs also in paraffin from bituminous shale (Krafft, *B.* 15, 1704; 21, 2256).

ENNDECANE DI-CARBOXYLIC ACID $C_{19}H_{38}(CO_2H)_2$. [90°]. From oxy-henicosoic acid $C_{19}H_{38}(CH_2OH)(CO_2H)$ by heating with soda-lime (Stärcke, *A.* 223, 312). White powder (from alcohol and light petroleum).

Salt.—PbA''.

ENNENOIC ACID $C_9H_{16}O_2$ *i.e.* $CPr_2:CH.CO_2H$. *Di-β-propyl-acrylic* acid. [81°]. From $Pr_2C(OH).CH_2.CO_2H$ and dilute H_2SO_4 (Albitzky, *J. pr.* [2] 30, 209). Needles (from benzene). Sl. sol. water, v. sol. alcohol, ether, and benzene.—LiA' 2aq.—BaA'_2 aq.—CaA'_2 aq. S. (of CaA'_2) 3·3 at 21°.—PbA'_2 2½aq.

Ennenoic acid $C_9H_{16}O_2$ *i.e.* $C_6H_{13}.CH:CH.CO_2H$. *Nonylenic acid.* Formed by heating heptoic aldehyde (œnanthol) with NaOAc and Ac_2O at 170° for 30 hours (Schneegans, *A.* 227, 80). Liquid, v. sl. sol. water, very volatile with steam. Readily combines with HBr forming bromoennoic acid (*q. v.*). Not attacked by nascent hydrogen.—BaA'_2.—CaA'_2 3aq: needles.—AgA'.

Ennenoic acid $C_9H_{16}O_2$. *Phoronic acid.* [169°]. $[\alpha_D] = 23°$ (in alcohol). Formed, together with camphic acid, by exposing sodium-camphor to the air (Montgolfier, *A. Ch.* [5] 14, 82). Tables (from alcohol). Insol. water and CS_2.

ENNENYL ALCOHOL $C_9H_{18}O$ *i.e.* $Pr.CH:CH.CH_2.CMe_2.OH$. *Di-methyl-isopropyl-allyl-carbinol.* (176°). $R_\infty = 72·27$. From dimethyl-allyl-carbinol (hexenyl alcohol), isopropyl iodide, and zinc (Dieff, *J. pr.* [2] 27, 364). Gives isobutyric acid on oxidation. Combines with bromine forming $C_9H_{18}Br_2O$.

Methyl ether $C_9H_{17}OMe$. (171°). S.G. $\frac{21·6}{4}$ ·8027. R_∞ 81·55. $KMnO_4$ gives methylated oxy-valeric acid, $CH_3O.C_4H_8.CO_2H$, and isobutyric acid (Kononowitz, *J. pr.* [2] 30, 400; *Bl.* [2] 43, 381).

ENNENYLCHLORIDE $C_9H_{17}Cl$. (175°–185°). From the alcohol and PCl_5 (Dieff).

ENNINENE C_9H_{16}. (136°). *Campholene.* Obtained from campholic acid by the action of P_2O_5 or by distilling with soda-lime (Delalande, *A.* 38, 340; Kachler, *A.* 162, 266).

Enninene C_9H_{16}. (135°–140°). From camphor and HI at 200° (Weyl, *B.* 1, 96).

ENNINYL ALCOHOL $C_9H_{16}O$ *i.e.* $(CH_2:CH.CH_2)_2.CEt.OH$. *Ethyl-di-allyl-carbinol.* (176°). S.G. $\frac{0}{0}$ ·8776; $\frac{17}{0}$ ·8637. C.E. (0°–17°) ·00095. From propionic ether, allyl iodide, and zinc (Smirensky, *J. pr.* [2] 25, 59).

n-**ENNOIC ACID** $C_9H_{18}O_2$. *Pelargonic acid. Nonylic acid.* Mol. w. 158. [13°]. (254° i.V.). S.G. $\frac{12·5}{4}$ ·9109; $\frac{15}{15}$ ·9103; $\frac{99}{4}$ ·8433. H.C. 1287352. M.M. 9·590 at 20° (Perkin, *C. J.* 45, 486; Longuinine, *A. Ch.* [6] 11, 222).

Occurrence.—In the volatile oil of *Pelargonium roseum* (Pless, *A.* 59, 54). In fusel oil from beet root (Perrot, *A.* 105, 64).

Formation. — 1. From heptyl-aceto-acetic ether and KOH (Jourdan, *A.* 200, 105).—2. By action of HNO_3 on oleïc acid (Redtenbacher, *A.* 59, 52), on stearolic acid (Limpach, *A.* 190, 297), and on oil of rue (Gerhardt, *A.* 67, 245).—3. By fusing hendecenoic acid $C_{11}H_{20}O_2$ with KOH (Krafft, *B.* 15, 1691).

Properties.—Oil at ordinary temperatures.

Salts.—CaA'_2.—BaA'_2: laminæ, sl. sol. hot water.—CuA'_2 [c. 258°].—ZnA'_2 [132°].—AgA'.

Methyl ether MeA'. (214° i.V.). S.G. $\frac{0}{0}$ ·8918. S.V. 245·7. C.E. (0°–10°) ·00091 (Gartenmeister).

Ethyl ether EtA'. (228° i.V.). S.G. $^{17·5}$ ·8655 (Zincke a. Franchimont, *A.* 164, 339; $\frac{15}{15}$ ·8703; $\frac{25}{25}$ ·8641. M.M. 11·571 at 18·2° (Perkin, *C. J.* 45, 503).

Chloride $C_9H_{17}OCl$. (220°) (Cahours, *C. J.* 3, 240).

Amide $C_9H_{17}ONH_2$. [93°] (Schalfejeff, *B.* 6, 1252); [99°] (Hofmann, *B.* 15, 984). Formed by heating ammonium ennoate at 230° under pressure.

Anhydride $(C_9H_{17}O)_2O$. [-5°] (Chiozza, *A.* 85, 231).

Nitrile $CH_3(CH_2)_7CN$. (215°). S.G. ^{16} ·786. From *n*-octyl iodide and KCN at 180° (Eichler, *B.* 12, 1888).

Iso-ennoic acid $C_9H_{18}O_2$ *i.e.* $CH_3(CH_2)_5CHMe.CO_2H$. (245° cor.). S.G. ^{18} ·9033. From its nitrile, which is obtained by acting on methyl-hexyl-carbinyl iodide (octyl iodide) with KCy (Kullhem, *A.* 173, 319). Oil.—NaA′aq: slender needles.—KA′.—CaA′$_2$ aq: needles (from alcohol).—CuA′$_2$*x*aq.—AgA′.

Ethyl ether EtA′. (214° cor.). S.G. ^{17} ·8641.

Nitrile $CH_3(CH_2)_5CHMe.CN$. (206°). S.G. ^{14} ·8187.

Amide $CH_3(CH_2)_5CHMe.CONH_2$. [91°] and [105°] (?).

Ennoic acid $CH_3.(CH_2)_4.CHMe.CH_2.CO_2H$. (232°). Got by heating heptyl-malonic acid (Venable, *B.* 13, 1652). Oil.

V. also Bromo-ennoic acid.

ENNYL ALCOHOL $C_9H_{20}O$. *Nonyl alcohol.* Mol. w. 144. (c. 188°). S.G. $^{18·5}$ ·855. From petroleum ennane (Lemoine, *Bl.* [2] 41, 163; *cf.* Pelouze a. Cahours, *A. Ch.* [4] 1, 5).

Acetyl derivative $C_9H_{19}OAc$. (c. 210°).

Ennyl alcohol $C_9H_{20}O$. (205°–212°). S.G. ^{14} ·847. From isoamyl isovalerate and sodium (Lourenço a. Aguiar, *Z.* 1870, 404).

Acetyl derivative $C_9H_{19}OAc$. (207°–213°).

Ennyl alcohol $Pr_2CEt.OH$. *Ethyl-di-propyl-carbinol* (Tschebotareff a. Saytzeff, *J. pr.* [2] 33, 195). (179·5° cor.) (T. a. S.); (176°) (Menschikoff, *J. pr.* [2] 36, 351). V.D. 143·5 (for 144). V. sl. sol. water. S.G. $\frac{20}{0}$ ·8331; $\frac{30}{0}$ ·8258. From di-propyl ketone, EtI, and Zn. Gives, on oxidation, CO_2, acetic acid, propionic acid, and butyric acid, also di-propyl ketone and ennylene.

Acetyl derivative. (c. 190°). S.G. $\frac{20}{0}$ ·8675.

Ennyl alcohol $C_6H_{13}.CHEt.OH$. (195°). S.G. $\frac{0}{4}$ ·839; $\frac{20}{4}$ ·825. From heptoic aldehyde (œnanthol) and $ZnEt_2$ followed by water (Wagner, *Bl.* [2] 42, 330). Gives ethyl hexyl ketone on oxidation.

Acetyl derivative $C_9H_{19}OAc$. (211°). S.G. $\frac{0}{4}$ ·878; $\frac{20}{4}$ ·861.

ENNYLAMINE $C_9H_{19}NH_2$. (191°). Formed by the action of NH_3 on the ennyl chloride derived from petroleum (Pelouze a. Cahours, *J.* 1863, 529; *A. Ch.* [4] 1, 5).

Ennylamine $C_9H_{19}NH_2$. (195°). Formed by the action of Br and KOH on the amide of decoic (capric) acid (Hofmann, *B.* 15, 773).—$B'_2H_2PtCl_6$.

ENNYL CHLORIDE $C_9H_{19}Cl$. (c. 182°) (Lemoine, *Bl.* [2] 41, 164); (196°) (Pelouze a. Cahours, *J.* 1863, 529). S.G. ^{16} ·899 (P. a. C.); $^{25·5}$ ·908 (L.). From petroleum ennane by chlorination.

Ennyl chloride $C_9H_{19}Cl$. (150°–160°). From the ennyl alcohol obtained from isoamyl isovalerate and Na (Lourenço a. Aguiar, *Z.* 1870, 404).

ENNYLENE C_9H_{18}. *Nonylene.* Mol. w. 126. (c. 135°). S.G. $^{18·4}$ ·853. From the ennyl chloride which is derived from petroleum (Lemoine, *Bl.* [2] 41, 163).

Ennylene C_9H_{18}. (138°). S.G. ^{22} ·743. From ethyl-dipropyl-carbinyl iodide and alcoholic KOH (Socoloff, *J. R.* 1887, 599).

Ennylene C_9H_{18}. (140°). Among the products of the action of $ZnCl_2$ on fusel oil (Wurtz, *A.* 128, 232).

Ennylene C_9H_{18}. (145°). S.G. $^{20·5}$ ·757. Formed by the action of lime on heptoic aldehyde (œnanthol) (Fittig, *A.* 117, 78).

Ennylene C_9H_{18}. (c. 147°). From paraffin, by strongly heating it (Thorpe a. Young, *A.* 165, 18).

Ennylene C_9H_{18}. (c. 149°). S.G. ·787. Occurs in oil of resin (Renard, *Bl.* [2] 39, 541).

Ennylene C_9H_{18} (153° cor.). S.G. ^{0} ·762. Obtained by distilling the lime soap made from train oil (Warren a. Storer, *Z.* 1868, 230).

Ennylene C_9H_{18}. (121°). S.G. ^{12} ·753. Found among the products of the distillation of bituminous shale (Laurent, *A.* 25, 285).

V. also the *Hexahydrides* of Cumene and Mesitylene.

DI-ENNYL-KETONE $C_{19}H_{38}O$ *i.e.* $(C_9H_{19})_2CO$. *Caprinone* [58°]. (above 350°). Obtained by distilling calcium decoate (caprate). Pearly laminæ (from alcohol). Gives decoic acid on oxidation (Grimm, *A.* 157, 270).

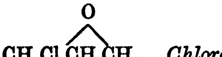
ENNYL - UREA *Decoyl derivative* $C_9H_{19}NH.CO.NH.CO.C_9H_{19}$. [101°]. White plates. Formed by the action of KOH on a mixture of the amide of decoic acid and bromine (Hofmann, *B.* 15, 761).

EOSIN *v. Tetra*-bromo-fluoresceïn.

EPIBROMHYDRIN C_3H_5BrO. (139°). S.G. ^{14} 1·615. From $C_3H_5Br_2(OH)$, and conc. KOHAq (Reboul, *A. Suppl.* 1, 227; Berthelot a. De Luca, *A. Ch.* [3] 48, 311). Formed also by distilling the compound of acetone with Br (Linnemann, *A.* 125, 310). NH_3 forms $C_6H_{12}BrNO_2$, an amorphous insoluble base.

Epidibromhydrin *v.* Di-bromo-propylene.

EPICHLORHYDRIN C_3H_5ClO *i.e.*



$CH_2Cl.\overbrace{CH.CH_2}^{O}$. *Chloro-propylene oxide.* Mol. w. 92½. (115·9°) (Schiff, *A.* 220, 99); (116·6 cor.) (Thorpe, *C. J.* 37, 207). S.G. $\frac{0}{4}$ 1·2031. C.E. (0°–10°) ·001033; (0°–100°) ·0011551. V.D. 3·21 (for 3·19). S.V. 87·1 (S.); 87·3 (T.).

Formation.—1. By treating di-chloro-propyl alcohol (glycerin dichlorhydrin) with fuming or gaseous HCl (Berthelot, *A. Ch.* [3] 41, 299). 2. By the action of alkalis on either of the two di-chloro-propyl alcohols $CH_2Cl.CHCl.CH_2OH$ or $CH_2Cl.CH(OH).CH_2Cl$ (Reboul, *A. Suppl.* 1, 221; Tollens a. Münder, *Z.* 1871, 252; Prevost, *J. pr.* [2] 12, 160; Claus, *B.* 10, 557: Cloëz, *A. Ch.* [6] 9, 145).

Properties.—Liquid with sweet taste, smelling like chloroform. Nearly insol. water, mixes with alcohol and ether.

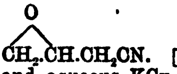
Reactions.—1. *Water* (½ vol.) at 100° converts it into chlorhydrin $CH_2Cl.CH(OH).CH_2(OH)$ and glycerin.—2. Fuming HCl readily acts upon it, forming $CH_2Cl.CH(OH).CH_2Cl$ (180°).—3. HBr forms $CH_2Cl.CH(OH).CH_2Br$ (197°). S.G. ^{12} 1·740. 4. HI acts with great violence, forming $CH_2Cl.CH(OH).CH_2I$ as well as propyl iodide and *n*-propyl chloride (Silva, *C. R.* 93, 418).—5. PCl_5 forms $CH_2Cl.CHCl.CH_2Cl$. PCl_3 forms $C_3H_5Cl_2(OPCl_2)$ (c. 136°) at 100 mm. (Hanriot, *Bl.*

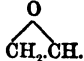
[2] 32, 551).—6. *Phosphorus pentabromide* gives $CH_2Cl.CHBr.CH_2Br$ (Darmstädter, *A.* 152, 319; *cf.* Wichelhaus, *A. Suppl.* 6, 277).—7. *Bromine* at 100° forms chloro-tri-bromo-acetone (Grimaux a. Adam, *Bl.* [2] 33, 257).—8. A solution of HClO (7 p.c.) in water in darkness produces $C_3H_6Cl_2O_2$ or $C_3H_4Cl_2(OH)_2$ (Carius, *A.* 134, 71). 9. *Acetyl chloride* in the cold, or more quickly at 100°, forms $C_3H_5Cl_2(OAc)$. By long heating (30 hours) at 100° there is also formed $C_6H_{10}Cl_3O(OAc)$ and $C_9H_{15}Cl_4O_2(OAc)$. *Butyryl chloride* forms $C_3H_5Cl_2(O.CO.Pr)$. *Benzoyl chloride* at 180° gives $C_3H_5Cl_2(OBz)$ (Truchot, *Bl.* [2] 5, 447; 6, 481).—10. *Acetic anhydride* at 180° gives $C_3H_5Cl(OAc)_2$ and $C_3H_5Cl_2(OAc)$ (T.; *cf.* Franchimont, *R. T. C.* 1, 43). Heating with *acetic acid* at 100° forms $C_3H_5Cl(OH)(OAc)$. *Benzoic anhydride* at 190° gives $C_3H_5(OBz)_3$ [74°] (Van Romburgh, *R. T. C.* 1, 46).—11. Conc. K_2SO_3Aq forms $C_3H_5(OH)(SO_3K)_2$ 2aq and free KOH (Pazschke, *Z.* [2] 5, 512).—12. $NaHSO_3$ at 100° forms $CH_2Cl.CH(SO_3Na)CH_2OH$ (Darmstädter, *Z.* [2] 4, 342).—13. *Alcohol* at 180° gives rise to $C_3H_5Cl_2(OH)$, $C_3H_5(OH)(OEt)_2$ and $C_3H_5Cl(OH)(OEt)$. *Isoamyl alcohol* at 220° forms $C_3H_5Cl(OH)(OC_5H_{11})$, $C_3H_5Cl_2(OH)$, and $C_3H_5(OH)(OC_5H_{11})_2$.—14. *Ethyl bromide* gives $C_3H_5ClBr(OEt)$.—15. *Sodium* forms a yellow oil $C_6H_{10}O_2$ (c. 218°), and an insoluble compound $C_6H_{10}O_2Na_2Cl_2$ (Hübner a. Müller, *A.* 159, 186; Hanriot, *Bl.* [2] 32, 552; Claus, *B.* 10, 556). 16. *Sodium ethylate* free from alcohol forms $C_3H_5(OH)(OEt)_2$ and white hygroscopic $C_{15}H_{28}O_5$ (Laufer, *Jena. Zeit.* [2] iii. 2 *Suppl.* 141; *cf.* Lourenço, *A. Ch.* [3] 67, 309).—17. Alcoholic KOPh forms crystalline $C_3H_5O(OPh)$ (Lippmann, *Sitz. W.* 62 [2] 605).—18. *Sodium amalgam* has little action, but forms a small quantity of allyl alcohol (Tornöe, *B.* 21, 1282; *cf.* Buff. *A. Suppl.* 5, 247).—19. H_2SO_4 forms oily $C_3H_5Cl(OH)(SO_4H)$ (Oppenheim, *B.* 3, 735).—20. Oxidised by HNO_3 to chloro-oxy-propionic acid.—21. Alcoholic or strong aqueous *ammonia* forms gummy $C_6H_{12}ClNO_2$(?) Gaseous ammonia reacts in the cold forming $N(C_3H_5Cl.OH)_3$ [93°] which forms a crystalline hydro-chloride [173°], and is converted by alkalis into a substance resembling gelatin (Fauconnier, *C. R.* 107, 115).—22. *Triethylamine* at 100° gives rise to crystalline $C_3H_5O.NEt_3Cl$ (Reboul, *C. R.* 93, 423).—23. *Aniline* at 140° forms oily $C_{15}H_{18}N_2O$, the constitution of which is probably $CH_2NHPh.CH(OH).CH_2.NHPh$. [54°] (290° at 10 mm.). It forms a hydrochloride $B''H_2Cl_2$ [202°] crystallising in needles, insol. ether, sol. alcohol and water, which gives the reactions usually characteristic of alkaloids (Fauconnier, *C. R.* 106, 605; 107, 250).—24. *Zinc* and *allyl iodide* followed by water give chloro-hexenoic acid (*q. v.*), the first reaction being represented thus: $C_3H_5ClO + Zn + IC_3H_5 = C_3H_5Cl(OZnI)C_3H_5$ (Lopatkine, *Bl.* [2] 41, 318).—25. HCN forms chloro-oxy-butyronitrile $C_3H_5Cl(OH)(CN)$, sol. water, alcohol, and ether (Hörmann, *B.* 12, 23).—26. KCy forms epicyanhydrin.—27. Boiling aqueous KCNO forms $C_4H_6ClNO_2$ [106°], crystallising in prisms (Thomsen, *B.* 11, 2136). It forms an acetyl derivative $C_4H_5AcClNO_2$ [79°].

Chlorinated epichlorhydrins *v.* CHLORO-ACETONE.

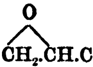
Epidichlorhydrin *v.* DI-CHLORO-PROPYLENE.

EPICYANHYDRIN C_4H_5NO *i.e.*



$\overset{O}{\widehat{CH_2.CH}}.CH_2CN$. [163°]. From epichlorhydrin and aqueous KCy (free from alkali) in the cold (Pazschke, *Z.* [2] 5, 512; *J. pr.* [2] 1, 82). Broad prisms (from water). Hot fuming HCl converts it into  $\overset{O}{\widehat{CH_2.CH}}.CH_2.CO_2H$ [225°] which, by further heating with fuming HCl for 6 hours at 160° is reduced to *n*-butyric acid (Hartenstein, *J. pr.* [2] 7, 295).

EPIIODHYDRIN C_3H_5IO *i.e.*



$\overset{O}{\widehat{CH_2.CH}}.CH_2I$. (160°–180°). S.G. ^{12} 2·03. From epichlorhydrin and KI at 100° (Reboul, *A. Suppl.* 1, 227). Oil.

EQUATIONS, CHEMICAL. The formula of an element expresses a certain quantity of that element, and the formula of a compound represents the composition of a certain quantity of that compound. When elements and compounds interact chemically, other elements and compounds are produced; a chemical equation represents, primarily, the quantities of the interacting bodies and the products of the interaction, and the compositions of these bodies. The sum of the quantities of the interacting bodies is equal to the sum of the quantities of the products of the interaction. A chemical equation then represents the distribution of the bodies which take part in a chemical change before the change begins and when the change is completed. But the equation does not give a full account of the transaction; thus the equation $Zn + H_2SO_4 = ZnSO_4 + H_2$ tells that, if zinc and sulphuric acid react to produce zinc sulphate and hydrogen, then 98 parts by weight of sulphuric acid react with 65·2 parts of zinc, and the quantities of zinc sulphate and hydrogen produced are represented by the numbers 161·2 and 2, respectively. The equation does not indicate the conditions which must be fulfilled in order that zinc and sulphuric acid shall react to produce zinc sulphate and hydrogen; as a matter of fact a considerable quantity of water must be present. Again, the equation $CaCl_2 + Na_2CO_3 = 2NaCl + CaCO_3$ merely asserts that when calcium chloride and sodium carbonate react to produce sodium chloride and calcium carbonate, for every 111 parts of calcium chloride changed 106 parts of sodium carbonate are also changed, but it does not tell that in order to effect the change of 111 parts of calcium chloride into calcium carbonate much more than 106 parts of sodium carbonate must be present although only 106 parts are actually chemically changed. An equation often represents a chemical occurrence as more simple than it really is. For instance, the equation $FeCl_3 + 3KCNS = Fe(CNS)_3 + 3KCl$ seems to imply that if 162·5 parts of ferric chloride were mixed with 291 parts of potassium sulphocyanide, 230 parts of ferric sulphocyanide and 223·5 parts of potassium chloride would be produced; but in order to change 162·5 parts of ferric chloride to ferric sulphocyanide something like 300 × 291 parts of potassium sulphocyanide must be present, although only 291 parts of the sulphocyanide are actually chemically changed.

The kinematical theories depend upon the conception which we owe to Clausius and Williamson, that in reversible chemical processes, such as the dissociation of a gas, the molecules of the gas are continually splitting up, and the atoms which are thus produced are continually recombining. When the state of equilibrium is reached the number of molecules decomposed in unit time must equal the number formed in the same time by the recombination of the atoms. Let us now consider the application of these principles to the simplest case of chemical combination we can choose, that of the dissociation of a diatomic gas into atoms. Since the molecules are continually splitting up, the time each molecule exists without decomposition is finite, and though this may vary from molecule to molecule the mean of such time will, however, be finite, and we shall call it the 'paired' time of the molecule and denote it by t_1. The mean time an atom remains alone and free from other atoms, we shall call the 'free' time, and denote it by τ'; since an atom in order to recombine must come close to another atom, the time an atom remains free will be inversely proportional to the number of collisions it has with other atoms, and therefore inversely proportional to the number of such atoms in unit volume. We may therefore put $\tau' = \frac{\tau}{n}$, where n is the number of free atoms in unit volume. To simplify the calculations, let us suppose that the time each molecule remains paired is the same for all molecules and equal to the paired time, and that the time an atom is free is the same for all atoms and equal to the free time. Then if N be the number of molecules in unit volume, the number of molecules which split up in a short time, δt, will be $\frac{N\delta t}{t_1}$, for we may suppose that the rate at which the molecules split up remains constant for the time t_1, but if so, N will split up during this time, so that the number which splits up in unit volume in the time δt will be $\frac{N\delta t}{t_1}$; similarly the number of atoms which pair in the time δt will be $\frac{n}{\tau'}\delta t$, that is $\frac{n^2}{\tau}\delta t$. Thus, if δN is the increase in time δt in the number of molecules in unit volume,

$$\delta N = \left(\frac{1}{2}\frac{n^2}{\tau} - \frac{N}{t_1}\right)\delta t$$

or

$$\frac{dN}{dt} = \frac{1}{2}\frac{n^2}{\tau} - \frac{N}{t_1};$$

similarly,

$$\frac{dn}{dt} = \frac{2N}{t_1} - \frac{n^2}{\tau}.$$

When the gas has reached a steady state $\frac{dN}{dt}$ and $\frac{dn}{dt}$ both vanish, so that

$$\frac{n^2}{N} = \frac{2\tau}{t_1} \quad . \quad . \quad (1)$$

From this expression we can find the vapour density of the gas when it is in the steady state. Let Δ be the density of the normal gas, and Δ' that of the dissociated gas at the same pressure; then, if S is the number of molecules in unit volume of the normal gas before dissociation,

$$\frac{\Delta'}{\Delta} = \frac{S}{N+n} = \frac{S}{S+\frac{n}{2}}.$$

Hence,

$$n = \frac{2S(\Delta - \Delta')}{\Delta'}$$

$$N = \frac{S(2\Delta' - \Delta)}{\Delta'}.$$

So that equation (1) becomes

$$\frac{2(\Delta - \Delta')^2}{(2\Delta' - \Delta)\Delta'} S = \frac{\tau}{t_1}.$$

But if the temperature remains constant S is proportional to the initial pressure p, so that we may write this equation as

$$\frac{p(\Delta - \Delta')^2}{(2\Delta' - \Delta)\Delta'} = (\text{a constant})\frac{\tau}{t_1} \quad . \quad . \quad (2)$$

The result that $\frac{p(\Delta - \Delta')^2}{(2\Delta' - \Delta)\Delta'}$ is constant, was obtained by Willard Gibbs from thermodynamical considerations, and was shown by him (*Am. S.* 17, 277) to agree with the results of experiments on the vapour densities at different pressures of nitrogen peroxide, and acetic and formic acids. More recently a most elaborate determination of the vapour density of nitrogen peroxide at different pressures has been made by E. and L. Natanson (*W. A.* 24, 454), with the result that at a constant temperature $\frac{p(\Delta - \Delta')^2}{(2\Delta' - \Delta)\Delta'}$ is constant. The preceding investigation shows that when a dissociable gas obeys this law $\frac{\tau}{t_1}$ must be independent of the density, and therefore, since τ does not depend upon the pressure, t_1 cannot do so; but if t_1 is independent of the pressure, the decomposition of the more complex molecules cannot be produced by collisions with molecules or atoms of the same kind, for if it were t_1 would diminish as the pressure increased. There does not appear to be any reason for supposing that on the kinetic theory of gases the collisions between the molecules must of necessity produce decomposition. There must be a limit to the velocity with which a particle is moving, for it is evident that the kinetic energy possessed by a single particle must be less than the kinetic energy in the smallest quantity of the gas which exhibits the property of the gas when in bulk. Thus, if a million molecules are sufficient to make the gas possess this property, the greatest value of the square of the velocity of a molecule would be a million times the velocity of mean square at this temperature, and therefore the square of the relative velocity of the atoms in a molecule after being struck by another molecule must be less than this value. The atoms in the molecule will not, however, part company unless the square of the relative velocity exceeds a certain value, depending upon the distance between the molecules, the law of force between them, and the intensity of this force at unit distance, so that the force may be so intense and the atoms so near that to split up the molecule the relative velocity of the atoms would have to be greater than that which could be produced by a collision with any molecule in the gas.

To return to formula (1), we see that if x denotes the ratio of the number of dissociated atoms, n, to S, the number of molecules originally present in unit volume, then

$$x^2 + x\frac{\tau}{t_1 S} = \frac{2\tau}{t_1 S} \quad . \quad . \quad (3)$$

or if only a small fraction of the molecules is dissociated

$$x^2 = \frac{2\tau}{t_1 S},$$

so that in this case the amount of dissociation is inversely proportional to the square root of the pressure.

By observing the amount of dissociation when the gas is in equilibrium, we can determine x, and hence by equation (3) $\frac{\tau}{t_1 S}$ or $\dfrac{\frac{x\tau}{n};}{t_1}$ this latter quantity is x times the ratio of the free to the paired time, so that by determining the vapour pressure of a gas when in a steady state, we can determine the ratio of its free to its paired time. Thus by comparing equation (3) with the result of Lemoine's experiments on the dissociation of HI, we find that, under atmospheric pressure, at 1250° the paired time is 1·32 times the free time, and at 900° only $\frac{1}{5}$. We cannot, however, by observations on the gas in the steady state determine the value of either of these times absolutely; if, however, we have determined their ratio in this way, we can, by observing the velocity of dissociation, determine the 'free' time of the atoms, for from equation (1) we have:

$$\frac{dn}{dt} = \frac{2\mathrm{N}}{t_1} - \frac{n^2}{\tau}$$
$$= \frac{2\mathrm{S} - n}{t_1} - \frac{n^2}{\tau}.$$

If we denote $\frac{\tau}{\mathrm{S}t_1}$ by c, which can be found by observations on the steady state of the gas, the solution of this differential equation, if

$$a = \mathrm{S}\left(2c + \frac{c^2}{4}\right)$$

is $\dfrac{1}{2a} \log \dfrac{(n + \frac{1}{2}\mathrm{S}c - a)}{n + \frac{1}{2}\mathrm{S}c + a} = -\dfrac{t}{\tau} + \text{constant},$

so that if t_1 is the time required for the number of atoms to increase from n_1 to n_2

$$\frac{1}{2a} \log \frac{(n_1 + \frac{1}{2}\mathrm{S}c - a)\,(n_2 + \frac{1}{2}\mathrm{S}c + a)}{(n_1 + \frac{1}{2}\mathrm{S}c + a)\,(n_2 + \frac{1}{2}\mathrm{S}c - a)} = \frac{t_1}{\tau} \quad (4)$$

Hence, if we observe the time taken for the dissociation of a known fraction of the gas we shall be able to find from this equation the 'free time,' and then, as from observations on the steady state we know the ratio of the paired to the free time, we can find the paired time.

The same principles can be applied to more complicated cases of equilibrium, such as the combination of hydrogen and iodine to form hydriodic acid. We shall suppose that the molecules of hydrogen and iodine and hydriodic acid are continually splitting up into atoms, and that these atoms are constantly recombining and forming molecules. In this case we have five things to consider, the hydrogen molecules and atoms, the iodine molecules and atoms, and the hydriodic acid molecules.

Let m and n be the number of hydrogen atoms and molecules respectively;
p and q the number of iodine atoms and molecules;
r the number of hydriodic acid molecules;
t_1, t_2, t_3, the times two atoms remain paired together in the hydrogen, iodine, and hydriodic acid molecules, respectively;
$\frac{\tau_1}{m}$, $\frac{\tau_2}{p}$ the times a hydrogen atom is free from a hydrogen and iodine atom respectively;
$\frac{\tau_3}{p}$ the time an iodine atom is free from another iodine atom;
M and N the total number of hydrogen and iodine atoms respectively, whether free or in combination with other atoms.

Then by the same reasoning as in the case of dissociation:

$$\frac{dm}{dt} = \frac{2n}{t_1} + \frac{r}{t_3} - \frac{2m^2}{\tau_1} - \frac{mp}{\tau_2}$$
$$\frac{dn}{dt} = \frac{m^2}{\tau_1} - \frac{n}{t_1}$$
$$\frac{dp}{dt} = \frac{2q}{t_2} + \frac{r}{t_3} - \frac{2p^2}{\tau_3} - \frac{mp}{\tau_2}$$
$$\frac{dq}{dt} = \frac{p^2}{\tau_3} - \frac{q}{t_2}$$
$$\frac{dr}{dt} = \frac{mp}{\tau_2} - \frac{r}{t_3}$$
$$m + 2n + r = \mathrm{M}$$
$$p + 2q + r = \mathrm{N}.$$

When the system has got into a steady state, m, n, p, q, r are all constant, so that the above equations may be written:

$$\frac{m^2}{\tau_1} = \frac{n}{t_1};\ \frac{p^2}{\tau_3} = \frac{q}{t_2};\ \frac{mp}{\tau_2} = \frac{r}{t_3} \quad . \quad . \quad (5)$$

In solving these equations we may assume that the number of free atoms of hydrogen or iodine is very small compared with the number of molecules; so that $n = \frac{1}{2}(\mathrm{M} - r)$ and $q = \frac{1}{2}(\mathrm{N} - r)$; hence from equation (5) we get:

$$\frac{\tau_2^2}{\tau_1\tau_3} r^2 = \frac{t_3^2}{4t_1t_2}(\mathrm{M} - r)(\mathrm{N} - r) \quad . \quad . \quad (6)$$

If equivalent quantities of hydrogen and iodine are present M = N and we have:

$$r = \left\{\frac{1}{4}\,\frac{t_3^2\tau_1\tau_3}{t_1t_2\tau_2^2}\right\}^{\frac{1}{2}}(\mathrm{M} - r).$$

In this case the ratio $\frac{r}{\mathrm{M}}$ is independent of the pressure.

Lemoine has made a very extensive series of experiments on the combination of hydrogen and iodine (*A. Ch.* [5] 11). In the following table the results of his experiments are compared with those given by equation (6); the value of $\frac{t_3^2\tau_1\tau_3}{t_1t_2\tau_2^2}$ being determined by making the observed and calculated results agree when N = M.

Combination of hydrogen and iodine at 440°.

Proportion of H + I.	Ratio of free hydrogen to the total quantity of hydrogen.	
	Observed.	Calculated.
H + I	·240	·240
H + ·784I	·350	·342
H + ·527I	·547	·519
H + ·258I	·774	·750

We see too from equation (6) that if M is very large compared with N, then $r = N$; that is, if the iodine is enormously in excess, the whole of the hydrogen is combined with iodine; in other other words there is no dissociation of the hydriodic acid; the effect of an excess of either hydrogen or iodine on the dissociation of HI is given by equation (6).

We could make other assumptions about the way in which the hydriodic acid was formed from the hydrogen and iodine which would lead to the same results for the equilibrium-condition, but which could be distinguished from the preceding assumptions by observations on the rate at which dissociation takes place. Thus we might suppose that the combination of hydrogen and iodine takes place by a molecule of hydrogen coming close to one of iodine, and that these molecules emerge from the collision as two molecules of hydriodic acid. The decomposition of the hydriodic acid might be supposed to be caused by two of its molecules coming into collision and emerging as two molecules of hydrogen and iodine. In this case, if n, q, r, represent the number of molecules of hydrogen, iodine, and hydriodic acid respectively, $\frac{m}{t_1}$ the time a molecule of iodine exists without combining with one of hydrogen, $\frac{r}{t_2}$ the time a molecule of hydriodic acid exists without combining with another to form two molecules of hydrogen and iodine; then

$$\frac{dr}{dt} = \frac{mq}{t_1} - \frac{r^2}{t_2},$$

and when there is equilibrium

$$mp = \frac{t_1}{t_2} r^2.$$

This is an equation of exactly the same form as that previously obtained on the other hypothesis, so that by observations on the equilibrium-condition we could not distinguish between them. The two hypotheses lead, however, to quite different expressions for the velocity with which various changes take place. Thus let us consider the rate at which a quantity of HI would dissociate according to the first hypothesis; in this case the initial rate of dissociation is given by

$$\frac{dr}{dt} = -\frac{r}{t_2},$$

according to the second

$$\frac{dr}{dt} = -\frac{r^2}{t_2}.$$

Thus according to the first hypothesis the quantity of hydriodic acid dissociated in a short time is proportional to the pressure, while according to the second it is proportional to the square of the pressure, so that the two hypotheses could readily be distinguished by observations on the rate of dissociation.

We can apply the above principles to any case of the combination of gases, but after what we have given, the reader will have no difficulty in making the investigation for himself, and we shall merely give the results.

Three monovalent gases, A, B, C, are mixed together; A can combine with both B and C to form the compounds AB and AC respectively, but B and C cannot combine; we wish to find how much of each compound is formed.

Let n, q, s, u, v, be the number of molecules in the steady state of A, B, C, AB, AC respectively, then we can prove

$$\begin{aligned} u^2 &= \alpha nq \\ v^2 &= \beta ns \end{aligned} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where α and β are constants, of which α does not depend upon C nor β upon B. Thus the number of molecules of the compound AB formed is proportional to the geometric mean of the number of free molecules of A and B, and similarly the number of molecules of the compound AC is proportional to the geometric mean of the number of free molecules of A and C.

We see from the equation that the same proportion of gases will enter into combination at all pressures. If M, N, P are the total number of atoms of A, B, C, respectively, in the vessel, then equation (7) may be written

$$\begin{aligned} u^2 &= \tfrac{1}{4}\alpha(M - u - v)(N - u) \\ v^2 &= \tfrac{1}{4}\beta(M - u - v)(H - v) \end{aligned} \quad . \quad . \quad (8)$$

hence $$\frac{u^2}{v^2} = \frac{N - u}{P - v}.$$

Suppose that C is largely in excess of A and B, then $P - v$ will be large compared with $N - u$, so that v must be large compared with u, that is, C absorbs practically the whole of A, and only a very small quantity of the compound AB is formed; if, however, both A and C are largely in excess of B then there is very little free B, the whole of it being converted into AB. Equation (8) enables us to find how much of each compound is formed when the substances are mixed in any proportions.

Another case we can solve by the same principles is when we have four substances, A, B, C, D, such that if their molecules are represented by {A}, {B}, {C}, {D}; the way they act on each other is expressed by the equation

$$\alpha\{A\} + \beta\{B\} = \gamma\{C\} + \delta\{D\},$$

the action being reversible; that is, A and B act on each other to produce C and D, and C and D act on each other so as to produce A and B. Then if p, q, r, s are the numbers of molecules of A, B, C, D respectively, we may prove by the method just described that

$$p^\alpha q^\beta = \kappa r^\gamma s^\delta \quad . \quad . \quad . \quad . \quad . \quad (9)$$

when κ is independent of p, q, r, and s. If $\alpha + \beta = \gamma + \delta$, that is, if the chemical action does not produce a change in the number of molecules, the relative amounts of the substances produced by the action will be independent of the pressure. If P, Q, P′, Q′ are the masses of A, B, C, D present initially, $\alpha\xi$, $\beta\xi$ the number of molecules of A and B which have disappeared, and $\gamma\xi$, $\delta\xi$ the number of molecules of A and B which have ap peared when equilibrium is reached, then equation (9) may be written

$$(P-\alpha\xi)^{\alpha}(Q-\beta\xi)^{\beta}=\kappa(P'+\gamma\xi)^{\gamma}(Q'+\delta\xi)^{\delta}\quad . \quad (10).$$

Thus if $P^{\alpha}Q^{\beta}$ is greater than $\kappa P'^{\gamma}Q'^{\delta}$, ξ is positive, that is, the A and B molecules combine to form C and D; but if $P^{\alpha}Q^{\beta}$ is less than $\kappa P'^{\gamma}Q'^{\delta}$, ξ is negative, that is, the C and D molecules combine to form A and B; thus the nature of the chemical action depends on the relative amounts of the combining substances initially present. This is an example of what is called *mass action*, which we shall consider more in detail in the following paragraph. For other examples of the application of this method we may refer to a paper by J. J. Thomson on chemical combination (*P. M.* 18, 232).

Guldberg and Waage's Theory.

A theory of chemical action based to some extent on kinematical principles was given by Guldberg and Waage in 1867 (*Études sur les Affinités Chimiques*), and an extended application in 1879 (*J. pr.* 19, 69); the results of this theory have been compared by the authors and others with the results of a large number of experiments. The theory may perhaps best be illustrated by considering a special case. Let us suppose that we have four soluble substances, A, B, C, D, in solution, and that these substances are such that A by its action on B produces C and D, while C by its action on D produces A and B; we may suppose that the four substances are hydrochloric acid, sodium nitrate, nitric acid, and sodium chloride. Let p, q, r, s be the masses of these substances, respectively, expressed in gram-equivalents, v being the volume in which they are contained, then $\frac{p}{v}, \frac{q}{v}, \frac{r}{v}, \frac{s}{v}$, are called by Guldberg and Waage the *active masses* of the four substances, and they assume that the amount of A and B which in unit time changes into C and D is proportional to the product of the active masses, and may be expressed by

$$\kappa\frac{p}{v}\frac{q}{v},$$

where κ is what they call the coefficient of affinity of A and B; similarly the amount of C and D which in unit time passes into A and B is

$$\kappa'\frac{r}{v}\frac{s}{v},$$

where κ' is the coefficient of affinity of C and D. When the system is in equilibrium the amount of A and B which passes into C and D in unit time must equal the amount of C and D which passes into A and B, so that

$$\kappa pq=\kappa' rs,$$

or if P, Q, R, S, are the amounts of A, B, C, D, initially present, and ξ is the number of equivalents of A and B which change into C and D, this equation may be written,

$$\kappa(P-\xi)(Q-\xi)=\kappa'(R+\xi)(S+\xi)\quad . \quad . \quad (11)$$

This is a quadratic equation to determine ξ; but we may easily show that it has only one admissible root, for if ξ is positive it must not be greater than the smaller of the quantities P and Q, and if negative it must not be greater than the smaller of the two quantities R and S. This root is given by

$$s=\frac{\kappa(P+Q)+\kappa'(R+S)}{2(\kappa-\kappa')}$$

$$\pm\sqrt{\left\{\frac{\kappa(P+Q+\kappa'(R+S)}{2(\kappa-\kappa')}\right\}^{2}+\frac{\kappa PQ-\kappa' RS}{\kappa-\kappa'}}$$

the + or − sign being taken according as $\kappa-\kappa'$ is negative or positive.

From equation (11) we see that if P is very much greater than Q, R, and S, $Q-\xi$ must be very small, that is, nearly the whole of B must combine; thus if we mix a large quantity of hydrochloric acid with smaller quantities of NaCl, HNO_3, $NaNO_3$, nearly the whole of the $NaNO_3$ will be changed into NaCl. Again, if κPQ is greater than $\kappa' RS$, ξ is positive, but if less, then ξ is negative; thus the way the reaction goes will depend upon the relative amounts of the combining substances initially present. Thus, if, in the case before considered, the amounts of HCl and $NaNO_3$ are large compared with those of NaCl and HNO_3, the reaction which goes on will be the conversion of $NaNO_3$ into NaCl and HNO_3; but if the quantities of HCl and $NaNO_3$ are small compared with those of NaCl and HNO_3 the reverse action will go on, and NaCl and HNO_3 will be converted into $NaNO_3$ and HCl. This effect of the quantities of the various substances in determining the nature of the chemical reaction is called *mass action*.

If we put $P=Q$, $R=0$, $S=0$, equation (11) becomes

$$\kappa(P-\xi)^2=\kappa'\xi^2.$$

Now if P and R are acids, Q and S salts, $\frac{\xi}{P-\xi}$ is the ratio in which the base divides itself between the acids A and B respectively, so that for this case $\frac{\kappa}{\kappa'}$ is the square of the ratio in which the base divides itself between the acids.

Comparison of Guldberg and Waage's Theory with Experiment.

Etherification.—Guldberg and Waage have compared their theory with the results of the experiments of Berthelot and St. Gilles upon etherification (*A. Ch.* [3] 65, 385; 66, 1; 68, 225). If A, B, C, D are respectively acetic acid, water, ether, and alcohol, they find $\frac{\kappa}{\kappa'}=4$. The observed and calculated effects of mixing these substances in different proportions is given in the following table:—

Initial quantities of				Quantity of acetic acid which enters into combination	
acetic acid	water	ether	alcohol	observed	calculated
P	Q	R	S	ξ	ξ
1	0	0	1	·665	·667
1	0	0	2	·828	·845
1	0	0	4	·902	·930
2	0	0	1	·858	·815
1	0	1·6	1	·521	·492
1	3	0	1	·407	·409
1	23	0	1	·116	·131
1	98	0	2	·073	·078

Division of a base between two acids. Thomsen's experiments. Thomsen, by measuring the thermal changes accompanying the reaction, was able to calculate the distribution of the masses (Thomsen's *Thermochemische Untersuchungen*, 1, 98). When A, B, C, D were respectively nitric acid, sodium sulphate, sulphuric acid, and sodium nitrate, Thomsen found that $\frac{\kappa}{\kappa'}=4$, and when they were mixed in different proportions the results were given in the following table, where $Q=1$, $R=0$, $S=0$: –

P equivalents of nitric acid + 1 equivalent of sodium sulphate :—

P	ξ	Heat absorbed	
		observed	calculated
$\frac{1}{8}$	·121	452	402
$\frac{1}{4}$	·232	808	828
$\frac{1}{2}$	·423	1292	1331
1	·667	1752	1773
2	·845	2024	1974
3	·903	2050	2019

The following tables, derived from Thomsen's experiments, are given by Guldberg and Waage (*J. pr.* 19, 87):—

Relative values of κ.

TABLE I.

Substance A	Substance D	κ
HCl	$NaCl$	1
HNO_3	$NaNO_3$	1
$\frac{1}{2}(H_2SO_4)$	$\frac{1}{2}(Na_2SO_4)$	·25
$\frac{1}{2}(H_2C_2O_4)$	$\frac{1}{2}(Na_2C_2O_4)$	·0676
H_3PO_4	NaH_2PO_4	·0625
$\frac{1}{2}(C_4H_6O_6)$	$\frac{1}{2}(C_4H_4Na_2O_6)$	·0025
$\frac{1}{3}(C_6H_8O_7)$	$\frac{1}{3}(C_6H_5Na_3O_7)$	·0025
$C_2H_4O_2$	$C_2H_3NaO_2$	·0009
HBO_2	$NaBO_2$	·0001

TABLE II.

Substance A	Substance D	κ
HCl	Chloride of a metal	1
$\frac{1}{2}(H_2SO_4)$	metal sulphate	·25

where the metal may be potassium, sodium, or ammonium.

TABLE III.

Substance A	Substance D	κ
HCl	Chloride of a metal	1
$\frac{1}{2}(H_2SO_4)$	metal sulphate	·5

where the metal may be Mg, Mn, Fe, Zn, Co, Ni, Cu. We see, therefore, that the value of $\frac{\kappa}{\kappa'}$ is almost independent of the nature of the base.

Ostwald repeated the experiments, using the change in volume of the solution to determine the distribution of the substances. The experiments are described and the results given in the art. AFFINITY (vol. i. p. 75).

Heterogeneous systems.—So far we have only considered those cases in which the four substances are in the same condition, being either all soluble or all gaseous; we can, however, apply the same considerations to the case when one of them, D suppose, is an insoluble solid. In this case if the extent of surface of D exposed to the solution does not alter, its active mass is constant; thus, using the same notation as before, we must regard s as constant, and then the equation becomes

$$\kappa pq=\kappa' rs,$$

or since s is constant,

$$(P-\xi)(Q-\xi)=c(R+\xi),$$

where c is $\frac{\kappa' s}{\kappa}$. This expression has been verified by W. Engel (*J. pr.* 19, 94) for the case where A, B, C, D were respectively oxalic acid, chloride of calcium, hydrochloric acid, and calcium oxalate. The results are given in the following table :—

1 equivalent of calcium chloride + P equivalents of oxalic acid.

Oxalic acid	Quantity of calcium oxalate precipitated	
	observed	calculated
P	ξ	ξ
·398	·385	·385
·596	·569	·568
·795	·744	·736
·994	·873	·863
1·491	·967	·961
1·988	·973	·979
1·000	·863	·864

If two of the four substances, B and D, are insoluble, then if the surfaces remain constant their active masses are constant, and the equation

$$\kappa pq=\kappa' rs$$

will become

$$(P-\xi)=c(R+\xi),$$

where c is a constant and equal to $\frac{\kappa' s}{\kappa q}$. This expression has been tested by Guldberg and Waage for two cases (*J. pr.* 91, 92). The first case is when A, B, C, D are respectively potassium sulphate, barium carbonate, potassium carbonate, and barium sulphate; they found that when the system had reached its state of equilibrium, the quantity of potassium sulphate was $\frac{1}{4}$ that of the potassium carbonate. The effect of mixing the substances in different proportions is given in the following table :—

Initial quantities of		Quantity combined	
potassium sulphate	potassium carbonate	observed	calculated
P	R	ξ	ξ
0	3·5	·719	·700
0	2·5	·500	·500
0	2	·395	·400
0	1	·176	·200
·25	2	·200	·200
·25	2·5	·300	·300
·25	3	·408	·400
·25	3·8	·593	·560
·50	2	trace	·000

The second case of this kind investigated by Guldberg and Waage was when A, B, C, D were respectively sodium sulphate, barium carbonate, sodium carbonate, and barium sulphate; they found that in this case when the system had reached its state of equilibrium the quantity of sodium sulphate was $\frac{1}{5}$ of the quantity of sodium carbonate. The effect of mixing the substances in various proportions is given in the following table:—

Initial quantity of		Quantity combined	
sodium sulphate	sodium carbonate	observed	calculated
P	R	ξ	ξ
0	5	·837	·833
0	3·5	·605	·583
0	2	·337	·333
0	1	·157	·167
·2956	3	·234	·254
·2956	3·86	·438	·396
·2956	4·10	·440	·437
·2956	4·73	·558	·543

The method we previously described will lead to the same results for the equilibrium of heterogeneous substances as Guldberg and Waage's method.

The preceding instances show that in a large number of cases Guldberg and Waage's formula $\kappa pq = \kappa' p' q'$ represents accurately the state of equilibrium; nevertheless as given by Guldberg and Waage the formula must be regarded as almost empirical. The reasoning they give is only applicable to the special case of combination when the two molecules A and B after coming into contact separate as two molecules of A′ and B′; the reasoning as they give it is not applicable to the case where the molecules of A and B have to split up into atoms before combination can take place, though if we use the kinematical method previously described we shall arrive at the same formula, in this case, if the chemical equivalents and the molecules are identical. The agreement of the formula with the experiments in some cases throws some light on the constitution of the molecules which take part in the reaction. Thus take the case represented by the equation

$$\underset{p}{H_2SO_4} + \underset{q}{2NaNO_3} = \underset{r}{2HNO_3} + \underset{s}{Na_2SO_4}$$

Now if the molecule of sodium nitrate is represented by $NaNO_3$, the molecule of H_2SO_4 has to come into collision with two molecules of $NaNO_3$ simultaneously for combination to take place, and the number of such collisions is proportional to pq^2. Again the number of collisions which can give rise to the reverse chemical action will be proportional to rs^2, so that for equilibrium

$$\kappa pq^2 = \kappa' rs^2.$$

If we compare this formula with Thomsen's experiments on this reaction we shall find that it does not agree at all well with the results, while the formula $\kappa pq = \kappa' rs$ does so. Again, if we consider the question from the dynamical point of view (*v.* p. 442) we shall also arrive at the equation $\kappa pq^2 = \kappa' rs^2$, if we assume that the molecule of sodium nitrate is represented by $NaNO_3$; if on the other hand we assume that the molecule is represented by $Na_2N_2O_6$, both methods lead to the equation $\kappa pq = \kappa' rs$, which is verified by experiment. Hence we conclude, either that the relative composition of the molecules is represented by the scheme H_2SO_4, $Na_2N_2O_6$, Na_2SO_4, $H_2N_2O_6$, or else that a salt solution is in no way analogous to a number of particles of the salt moving about in a volume equal to that of the solvent. It may be well to remark that we cannot get over the difficulty by assuming the above reaction to take place in two stages, thus

$$H_2SO_4 + NaNO_3 = HNaSO_4 + HNO_3$$
$$HNaSO_4 + NaNO_3 = Na_2SO_4 + HNO_3.$$

Ostwald's researches (*v.* AFFINITY) show that the ratio in which a base divides itself between two acids is generally independent of the nature of the base, though if one of the acids is H_2SO_4 there are exceptions to this rule. We may therefore regard κ as the product of two factors α and β, of which α depends only upon the acid and β only upon the base, while κ' will be the product of β and another factor α' which depends only on the other acid; the ratio of κ to κ' will then be the same as the ratio of α to α', and will depend only upon the acids. If we apply the method given on p. 436 to this case we can see how this may be brought about. Let us consider the reaction

$$HCl + NaNO_3 = HNO_3 + NaCl.$$

Let p, q, r, s be the number of molecules of HCl, $NaNO_3$, HNO_3, and NaCl respectively, t_1, t_2, t_3, t_4, the paired time of these molecules, and let x, y, z, w be the number of free atoms of H, Cl, NO_3, and Na respectively, $\frac{y}{\tau_1}$ the time an atom of H is free from one of Cl, $\frac{3}{\tau_3}$ the time an atom of H is free from one of NO_3, $\frac{w}{\tau_4}$ the time an atom of Cl is free from one of Na, and $\frac{w}{\tau_2}$ the time an atom of NO_3 is free from one of Na; then, by the method on p. 437, we have the following equations:—

$$\frac{dp}{dt} = \frac{xy}{\tau_1} - \frac{p}{t_1}$$
$$\frac{dq}{dt} = \frac{zw}{\tau_2} - \frac{q}{t_2}$$
$$\frac{dr}{dt} = \frac{xz}{\tau_3} - \frac{r}{t_3}$$
$$\frac{ds}{dt} = \frac{wy}{\tau_4} - \frac{s}{t_4}$$

So that when there is equilibrium

$$\frac{\tau_1 \tau_2}{t_1 t_2} pq = \frac{\tau_3 \tau_4}{t_3 t_4} rs \quad . \quad . \quad (12)$$

τ_2, τ_4, t_2, t_3 are the only quantities which depend upon the base. We may regard the salt as made up of two systems, the radicle and the base, held together by forces between them; these forces will depend upon the relative configuration of the two systems, and we may suppose that this force vanishes when the two systems have simultaneously the configurations α and β. Now if T_1, T_2 are the times of vibrations of the systems about the configurations α and β respectively, the time which elapses between the two systems leaving this configuration and entering it again will, if

T_1 and T_2 are incommensurable, be $T_1 \times T_2$, so that if the system can get into the state in which the force between them vanishes, the longest time they can exist without doing so will be $T_1 \times T_2$, and thus the paired time will be proportional to $T_1 \times T_2$. The two systems will probably vibrate approximately as if they were free, so that, approximately, T_1 will only depend upon the radicle and T_2 on the base; thus, since the base in NaCl is the same as in $NaNO_3$, the ratio of t_2 to t_4 will be independent of the base. Again, when the base and radicle come together again after having been dissociated, the force between them will depend upon their configuration, and we may suppose that unless the atoms are in certain configurations the force between them will not be sufficient to cause them to enter into combination. If T_1', T_2' are the times of vibration of the radicle and the base about these configurations, the time which will elapse between the systems leaving this configuration and entering it again will be $T_1' \times T_2'$, the longer these intervals are separated the less chance will there be of the system entering into combination, and the free time will be proportional to $T_1' \times T_2'$; since one of these factors depends only on the base, and the other only upon the radicle, $\frac{\tau_2}{\tau_4}$ will be independent of the base, and therefore by equation (12) the proportion in which the base divides itself between the two acids will be independent of the base. (For another method, partly kinematical, *v.* Pfaundler, *P. Jubelbd.* 182, 131, 55.)

DYNAMICAL METHODS.

In any dynamical system in a steady state there is a certain quantity called the Lagrangian Function (T − V, where T and V are respectively the mean kinetic and potential energies of the system) which reaches a maximum value when the system is in a steady state, and the knowledge of the expression for this quantity enables us to determine the configuration of the system when in this state. Exactly the same thing holds for the physical and chemical systems whose equilibrium we are now considering. It may be proved (see *Applications of Dynamics to Physics and Chemistry*, J. J. Thomson, chap. ix.) that when such systems are in a steady state their mean Lagrangian Function has a maximum value, and that all the circumstances of the equilibrium can be obtained by making use of this property. We shall for brevity call the mean Lagrangian Function, the quantity which has this property, the 'directrix' of the system, as the behaviour of the system is entirely regulated by this function.

The directrix is closely analogous to what in thermodynamics is called the entropy of the system, and the theorem that in the steady state the 'directrix' is a maximum is analogous to Clausius' theorem that the entropy of the system tends to a maximum. Willard Gibbs (*Equilibrium of Heterogeneous Substances; Am. S.* 16, 442), Horstmann (*B.* 12, 64), Liveing (*Chemical Equilibrium the result of the degradation of Energy*) (Planck, *W. A.* 30, 562; 31, 189; 32, 462), have treated the subject of chemical equilibrium from this point of view. As the problems can, however, be solved by purely mechanical principles it seems preferable to do so. Though we can obtain the conditions of equilibrium both from mechanical principles and from the Second Law of Thermodynamics, it does not follow that we can therefore deduce the Second Law of Thermodynamics entirely from mechanical principles. The Second Law of Thermodynamics consists of two parts: one, that every distribution of heat tends to uniformity, by heat passing from places of higher to places of lower temperature; the other, that the entropy is a perfect differential; the second of these statements, but not the first, can be proved by purely dynamical principles. It must be remembered that what we show is that if the system does reach a steady state, the directrix must be a maximum; we cannot, however, prove that it must reach this state; this has to be deduced from observation.

In order to apply this method to find the conditions of equilibrium for chemical systems, we shall require the expressions for the directrix both for a mass of gas and a mass of liquid. If L_1 be the directrix for a mass ξ of a gas, which obeys Boyle's Law, and whose density is ρ, and absolute temperature θ, then (J. J. Thomson, *Applications of Dynamics*, chaps. x. and xi.)

$$L_1 = \xi R_1 \theta \log \frac{\rho_0}{\rho} + \xi A\theta + \xi B\theta \log \theta - \xi V_1 \quad . \ (13)$$

where R_1 is the value of $\frac{p}{\rho\theta}$, p being the pressure; ρ_0, A, and B are constants, and V_1 is the mean potential energy of the molecules of unit mass of the gas.

The directrix L_2 of a mass η of liquid, free from strain, electrification, &c., is given by the equation

$$L_2 = \eta\phi(\theta) - \eta V_2 \quad . \quad . \quad . \ (14)$$

when $\phi(\theta)$ is a function of the temperature, and V_2 is the mean potential energy of the molecules of unit mass of the liquid. If the liquid is strained or electrified, or if it possesses energy in virtue of its surface tension, we can easily calculate the correction to the directrix; for, since the directrix is $\bar{T}-\bar{V}$, all that we have to do is to calculate the potential energy arising from the strain, &c., and subtract it from the expression (14). Thus if the liquid is strained we must subtract from (14) $\frac{1}{2}kV_0\sigma^2$, where k is the bulk modulus of the liquid, V_0 its volume when unstrained, and σ is the compression; again if the liquid has a free surface it will possess potential energy in virtue of its surface tension, equal to ST when S is the area of the surface and T the surface tension; to get the directrix in this case we must, therefore, subtract ST from the value given by (14).

To illustrate the method of solving problems by this principle, let us take the case of the evaporation of a liquid in a closed vessel. We have here two systems to consider: the vapour and the liquid; if ξ is the mass of the vapour, which we shall assume to obey Boyle's Law, its directrix L_1 is given according to (13) by

$$L_1 = \xi R_1 \theta \log \frac{\rho_0}{\rho} + \xi A\theta + \xi B\theta \log \theta - \xi V_1;$$

while if η is the mass of the liquid, its directrix L_2 is given by

$$L_2 = \eta\phi(\theta) - \eta V_2;$$

and if Δ is the directrix of the whole system,

$$\Delta = L_1 + L_2.$$

When the system is in equilibrium Δ must be a maximum, so that if we suppose a mass $\delta\xi$ of the liquid to evaporate we must have in the state of equilibrium

$$\frac{d\Delta}{d\xi} = 0 \qquad . \quad . \ (15)$$

Since the sum of the masses of the vapour and liquid is constant $\frac{d\eta}{d\xi} = -1$, so that equation (15) leads to the relation

$$R\theta\log\frac{\rho_0}{\rho} + R\theta\frac{\rho}{\sigma} + A\theta + B\theta\log\theta - \phi(\theta) - (v_1 - v_2) = 0 \qquad (16)$$

where σ is the density of the liquid. This gives the expression for the vapour density ρ of the liquid at the temperature θ.

It may be well to consider this case more in detail. Let us suppose that we start with some of the liquid and no vapour: then the system will move so as to increase the directrix; now at first when $\rho = 0$ the rate of increase of L_1 with ξ is infinitely great, so that Δ will increase if a small quantity of the liquid evaporates, and therefore, by the principle just stated, evaporation will take place; as more liquid evaporates the rate of increase of L_1 gets smaller and smaller, until a point is reached where the increase in the directrix of the vapour, when a small quantity of the liquid evaporates, equals the diminution of the directrix of the liquid under the same circumstances; when this point is reached the directrix will be a maximum and the system will remain in this state. If the external circumstances alter so as to affect the rate of change of the directrix of either the vapour or liquid as evaporation goes on, it will alter the point at which equilibrium is reached. Thus, for example, suppose that the liquid is in the form of a spherical drop: then, in virtue of its surface tension, it will possess potential energy proportional to its surface; when it evaporates, the surface, and therefore the potential energy, will diminish; but since the directrix of the liquid is $\overline{T} - \overline{V}$, the diminution in the potential energy of the liquid when it evaporates will cause the directrix to diminish more slowly with evaporation than it would if the liquid were of such a form that the area of its surface did not change on evaporation. The evaporation will, therefore, have to go on further than before, in order that the rate of increase of the directrix of the vapour shall sink to that of the rate of diminution in the directrix of the liquid. The vapour pressure, therefore, when there is equilibrium will be greater when the liquid is in the form of drops than when its surface is plane. If the drop, however, had been electrified, then, since the electricity is not carried away by the vapour, the potential energy of the liquid will increase as evaporation goes on, and the drop gets smaller, so that the same reasoning as before will show that the vapour pressure over an electrified drop is less than over one which is not electrified. These cases are examples of a corollary from the principle we are considering, which may be stated generally by saying that when the physical environment of a system is changed, and the consequent change in the directrix of the system increases as any physical process goes on, then this process will have to go on further in the changed state before equilibrium is reached than in the unchanged one, while if the change in the directrix diminishes as the process goes on it will not have to proceed so far. The principle that the directrix is a maximum in equilibrium readily enables us to calculate the change made in the extent to which the process goes on. Thus, in the case of evaporation, if χ is the change in the directrix caused by any change in the conditions, $\delta\rho$ the consequent change in the vapour pressure when there is equilibrium, then we can easily show that

$$\delta\rho = \frac{1}{R\theta}\,\frac{\rho\sigma}{\sigma - \rho}\,\frac{d\chi}{d\xi}.$$

In the case of the spherical drop, χ is minus the potential energy due to surface tension, or if a be the radius $-4\pi a^2T$, and since $\frac{da}{d\xi} = -\frac{1}{4\pi a^2\sigma}$ we get

$$\delta\rho = \frac{2\rho}{\sigma - \rho}\,\frac{T}{a}\,\frac{1}{R\theta}.$$

Dissociation.—We can apply the same principles to cases of dissociation: let us suppose that we have a gas A which dissociates into two others, B and C; let ξ, η, ζ be the masses of these gases; ρ_1, ρ_2, ρ_3 their densities; v_1, v_2, v_3 the mean potential energy of unit mass of their molecules; R_1, R_2, R_3, the values of $\frac{p}{\rho\theta}$ for the three gases respectively; then if L_1, L_2, L_3 are the directrices of the three gases

$$L_1 = \xi R_1\theta\log\frac{\rho_0}{\rho_1} + \xi A_1\theta + \xi B\theta\log\theta - \xi V_1;$$

with corresponding expressions for L_2 and L_3. Δ, the directrix of the whole system, is given by the equation

$$\Delta = L_1 + L_2 + L_3;$$

if v is the volume in which the gases are confined $\rho_1 = \frac{\xi}{v}$, $\rho_2 = \frac{\eta}{v}$, $\rho_3 = \frac{\zeta}{v}$. When the system has reached equilibrium, Δ is a maximum and therefore $\frac{d\Delta}{d\xi}$ is zero, if c_1, c_2, c_3 are the combining weights of the gases A, B, C,

$$\frac{d\eta}{d\xi} = -\frac{c_2}{c_1} \text{ and } \frac{d\zeta}{d\xi} = -\frac{c_3}{c_1}.$$

So that the condition

$$\frac{d\Delta}{d\xi} = 0$$

leads to the equation

$$R_1\theta\log\frac{\rho_0{}^{\mathrm{I}}}{\rho_1} - \frac{c_2}{c_1}R_2\theta\log\frac{\rho_0{}^{\mathrm{II}}}{\rho_2} - \frac{c_3}{c_1}R_3\theta\log\frac{\rho_0{}^{\mathrm{III}}}{\rho_3}$$

$$-\left(R_1\theta - \frac{c_2}{c_1}R_2\theta - \frac{c_3}{c_1}R_3\theta\right) + \left(A_1 - \frac{c_2}{c_1}A_2 - \frac{c_3}{c_1}A_3\right)\theta$$

$$+\left(B_1 - \frac{c_2}{c_1}B_2 - \frac{c_3}{c_1}B_3\right)\theta\log\theta - \left(v_1 - \frac{c_2}{c_1}v_2\right.$$

$$\left. - \frac{c_3}{c_1}v_3\right) = 0,$$

or since

$$c_1R_1 = c_2R_2 = c_3R_3$$

this may be written

$$\frac{\eta\zeta}{\xi v} = C\theta^{a} e^{\frac{\left(v_1 - \frac{c_2}{c_1} v_2 - \frac{c_3}{c_1} v_3\right)}{R_1 \theta}} \quad . \quad . \quad (17)$$

Where C and a are constants, in the case of the dissociation of an elementary gas into atoms, we must suppose B and C to be the same, so that $\eta = \zeta$, $c_2 = c_3 = \frac{1}{2} c_1$; thus equation (17) reduces to

$$\frac{\eta^2}{\xi v} = C\theta^{a} e^{\frac{v_1 - v_2}{R_1 \theta}} \quad . \quad . \quad (18)$$

This equation is the same as that which we previously obtained from kinematical principles, but expresses in addition the way the dissociation varies with the temperature. Formulæ derived from thermodynamical principles have been given by Willard Gibbs (*Equilibrium of Heterogeneous Substances*, p. 169) and Boltzmann (*W. A.* 22, 39). In Willard Gibbs's formula a is equal to -1, and in Boltzmann's it is equal to zero. Natanson's experiments on the dissociation of N_2O_4 show that neither of these values of a agrees well with the observations. We see from (17) that if we have given masses of the substances, $\frac{\eta\zeta}{\xi}$ is proportional to v, so that the greater the volume in which the gas is contained the greater is the dissociation. The effect of an excess of one of the products of the dissociation (*v.* art. DISSOCIATION) follows at once from (17).

$\frac{c_3}{c_1} v_3 + \frac{c_2}{c_1} v_2 - v_1$ is the increase in the potential energy when unit mass of the gas dissociates; it may be approximately measured by H, the amount of heat which must be supplied to the system to keep the temperature constant when unit mass dissociates; when dissociation is accompanied by an absorption of heat, H is positive, when by an evolution, H is negative. Introducing H into equation (17) we get

$$\frac{\eta\zeta}{\xi v} = C\theta^{a} e^{-\frac{H}{R_1 \theta}} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

so that if H be positive $\frac{\eta\zeta}{\xi v} = 0$ when θ is 0, and, therefore, either η or ζ must vanish, so that at the absolute zero of temperature there is no dissociation; when θ is infinite $\frac{\eta\zeta}{\xi v}$ is infinite if a be positive, *i.e.* ξ must vanish, and therefore all the gas be dissociated; if a be zero $\frac{\eta\zeta}{\xi v}$ is finite, and there is a finite amount of dissociation; and if a be negative $\frac{\eta\zeta}{\xi v}$ is zero, and there is again no dissociation. We see from (18) that the greater the thermal changes accompanying dissociation, other circumstances being the same, the smaller will be the amount of dissociation at a given temperature.

Dilute solutions.—So far we have only considered gases, but Van 't Hoff (*L'Equilibre chimique dans les systèmes gazeux ou dissous à l'état dilué*, *Archiv. Néerlandais*, 20, 239 [1887]) has pointed out that Pfeffer's experiments on the osmotic pressures produced by salts dissolved in water (Pfeffer, *Osmotische Untersuchungen*, Leipzig, 1887), and Raoult's experiments on the effect of dissolved salts on the freezing points of solutions (*A. Ch.* [6] 4, 401), show that the molecules of a salt in a dilute solution exert the same pressure as they would exert if they were in the gaseous state at the same temperature, and occupying a volume equal to that of the liquid in which the salt is dissolved, and that the pressure exerted by these molecules obeys Boyle's and Gay-Lussac's laws. This being so, the directrix for the salt dissolved in the liquid must be the same as that for an equal mass of gas filling the volume occupied by the liquid. The preceding remarks are strictly true for such solvents as benzene or alcohol, but when the solvent is water there are many exceptions to them; most inorganic acids and salts behave as if they exerted a greater pressure than this rule would indicate, and it has been suggested by Arrhenius that this is due to the dissociation of the salt in the solution, though in some cases it would be necessary to suppose that dissociation amounted to more than 95 p.c in order to explain the effect. We must remember that this representation of the behaviour of a solution is founded on the hypothesis that the solvent merely sustains the particles of the salt or acid, and it would require to be modified if anything analogous to chemical combination took place between the salt and the solvent; as such combinations do undoubtedly in many cases take place, it does not seem necessary to call in the aid of extreme dissociation until it has been shown that the effects could not be explained as due to the chemical action between the salt and the water. The fact that in order to produce comparable osmotic pressures it is necessary to have in the solution the same number of chemical equivalents rather than the same number of molecules points also to this explanation. If we assume that the directrix of the dissolved salt is the same as that of an equal mass of the substance when gaseous and occupying the same volume, it is easy to calculate the conditions of chemical equilibrium between them. For, let us take the case where we have dilute solutions of four substances A, B, C, D, such that when A acts upon B it produces C and D, and when C acts upon D it produces A and B. Let $\{A\}$, $\{B\}$, $\{C\}$, $\{D\}$ represent the molecules of A, B, C, D respectively, and let the chemical action which takes place be represented by the equation

$$a\{A\} + b\{B\} = c\{C\} + d\{D\}.$$

Let ξ, η, ζ, ϵ represent the masses of these substances respectively, and let the directrices be

$$\xi R_1 \theta \log \frac{v\rho_0'}{\xi} + \xi(A_1\theta + B_1\theta \log \theta) - \xi w_1$$

$$\eta R_2 \theta \log \frac{v\rho_0''}{\eta} + \eta(A_2\theta + B_2\theta \log \theta) - \eta w_2$$

$$\zeta R_3 \theta \log \frac{v\rho_0'''}{\zeta} + \zeta(A_3\theta + B_3\theta \log \theta) - \zeta w_3$$

$$\epsilon R_4 \theta \log \frac{v\rho_0''''}{\epsilon} + \epsilon(A_4\theta + B_4\theta \log \theta) - \epsilon w_4,$$

where v is the volume of the solvent, let Q represent the directrix of the solvent, w_1, w_2, w_3, w_4, being the potential energies of unit masses of the substances. If c_1, c_2, c_3, c_4 are the combining weights of the four substances, and $d\xi$,

$d\eta$, $d\zeta$, $d\epsilon$ are corresponding increments in their masses; then the increments in the number of molecules of each of the substances are proportional to $\frac{d\xi}{c_1}$, $\frac{d\eta}{c_2}$, $\frac{d\zeta}{c_3}$, $\frac{d\epsilon}{c_4}$; but by the nature of the reaction which goes on between these substances, the increments in the number of molecules must be proportional to a, b, $-c$, $-d$, so that we have

$$\frac{d\xi}{ac_1} = \frac{d\eta}{bc_2} = -\frac{d\zeta}{cc_3} = -\frac{d\epsilon}{dc_4},$$

or

$$\frac{d\eta}{d\xi} = \frac{bc_2}{ac_1},\ \frac{d\zeta}{d\xi} = -\frac{cc_3}{ac_1},\ \frac{d\epsilon}{d\xi} = -\frac{dc_4}{ac_1} \qquad (19)$$

Then, since in equilibrium the directrix is a maximum, $\frac{d\Delta}{d\xi}$ must vanish; from this condition, and remembering equation (19), and that $R_1c_1 = R_2c_2 = R_3c_3 = R_4c_4$, we get

$$\frac{\zeta^c\epsilon^d}{\xi^a\eta^b} = \phi(\theta)v^{c+d-a-b}\,e^{\frac{a}{R_1\theta}\frac{dw}{d\xi}}\,e^{-\frac{a}{R_1\theta}\frac{dQ}{d\xi}} \qquad (20)$$

when $\phi(\theta)$ is a function of the temperature, and $w = \xi w_1 + \eta w_2 + \zeta w_3 + \epsilon w_4$.

The value of $\frac{dQ}{d\xi}$ will be zero if the properties of the solvent do not change as chemical action goes on; in any case since the solutions are very dilute the properties of the solvent may be assumed to be changed by an amount proportional to the quantity of the salt dissolved, so that Q will be a linear function of ξ, η, ζ, ϵ, and therefore $\frac{dQ}{d\xi}$ will be independent of ξ; thus the existence of the term involving Q will not modify the form of the equation, but is at most equivalent to a slight alteration in the value of $\frac{dw}{d\xi}$, the increase in the potential energy of the system when the mass of ξ is increased by unity. It may be shown (*v.* J. J. Thomson, *Applications of Dynamics to Physics and Chemistry*, p. 278) that

$$\phi(\theta) = c\,\theta^{\frac{1}{R_1c_1}(as_1c_1+bs_2c_2-cs_3c_3-es_4c_4)}$$

where s_1, s_2, s_3, s_4 are the specific heats of the substances A, B, C, D respectively.

Equation (20) will enable us to find the effects of pressure and temperature upon chemical combination.

Effect of pressure.—From equation (20) we see that, if $a+b=c+d$, then $\frac{\zeta^c\epsilon^d}{\xi^a\eta^b}$ is independent of the volume; but if $a+b=c+d$, the number of the molecules is not altered by the chemical reaction, so that in this case the amount of combination is independent of the pressure; if $a+b$ is greater than $c+d$, then the greater the volume v the smaller is the ratio $\frac{\zeta^c\epsilon^d}{\xi^a\eta^b}$. Now, the action of C upon D tends to diminish this ratio, while that of A on B tends to increase it, and if $a+b$ is greater than $c+d$ the number of molecules is increased when C acts upon D and diminished when A acts upon B. Thus, when chemical combination alters the number of molecules, the state of equilibrium depends upon the volume of the solvent, and the effect of increasing the volume is to favour that reaction which is attended by an increase in the number of molecules. In other words, the chemical action which produces an increase in volume is hindered by pressure, while that which produces a diminution is helped by it. This is an example of the corollary stated on p. 443.

Effect of temperature.—In equation (20) $\frac{dw}{d\xi}$ represents the increment in the potential energy of the system when ξ is increased by unity, and may be approximately measured by the amount of heat given out when ξ diminishes by unity; if the combination of C and D is accompanied by the production of heat, $\frac{dw}{d\xi}$ is negative, and therefore, when θ is zero, $\frac{\zeta^c\epsilon^d}{\xi^a\eta^b}$ is zero too, and therefore either ζ or ϵ must vanish; that is, the combination of C and D goes on until one of the components is exhausted; in other words, the reaction which is attended with the production of heat will go on as far as possible.

According to Berthelot's law of maximum work the reaction accompanied by the formation of heat goes on as far as possible at all temperatures; we see, however, from equation (20) that in reality it only does so at the absolute zero of temperature, though, if the reaction is accompanied by large thermal effects, the law will be an approximation to the truth for a considerable range of temperature.

This equation shows, too, that if there is any thermal effect at all, the relative affinities of two acids at the absolute zero of temperature is either zero or infinity.

If the substances obey Dulong and Petit's law

$$s_1c_1 = s_2c_2 = s_3c_3 = s_4c_4 = \overline{w}, \text{ say};$$

and then

$$\frac{\zeta^c\epsilon^d}{\xi^a\eta^b} = c\,\theta^{\frac{w}{R_1c_1}(a+b-c-d)}\,e^{\frac{a}{R_1\theta}\frac{dw}{d\xi}}.$$

If $a+b$ is greater than $c+d$, then $\frac{\zeta^c\epsilon^d}{\xi^a\eta^b}$ is infinite when θ is infinite, that is, the reaction accompanied by a diminution in volume goes on as far as possible at an infinitely high temperature. If $a+b=c+d$, that is, if the combination does not change the volume, the combination will only be partial at an infinitely high temperature.

We saw that Ostwald's experiments showed that in the case of an acid and two bases the value of

$$\frac{\left(\frac{\zeta}{c_3}\right)^c\left(\frac{\epsilon}{c_4}\right)^d}{\left(\frac{\xi}{c_1}\right)^a\left(\frac{\eta}{c_2}\right)^b}$$

was independent of the nature of the base; equation (20) shows that for this to be the case the amount of heat given out, when the number of molecules of one of the salts increases by unity and that of the other diminishes by the same amount, must be independent of the nature of the base. Now Thomsen's thermochemical researches have shown that the heat of formation of a salt seems to be the sum of two parts (*v.* Lothar Meyer, *P. M.* 23, 504), one of which depends only on the base and the other only on the acid. Thus, in the reactions of the kind we are considering, where we have two salts of the same base, one of which is formed while the other disappears, the thermal effects will be independent of the nature of the base. We see, therefore, that thermochemical investigations confirm Ostwald's results.

The greater the thermal effects which accompany the reaction the more rapidly will the conditions of equilibrium vary with the temperature.

By the principle enunciated on p. 442 we can readily find the effect of any alteration in the physical conditions on the amount of chemical combination which must take place before equilibrium is reached. Thus, take for example the effect of surface tension; if the energy due to the surface tension increases as a chemical action proceeds, then the larger the surface of the solution the smaller is the amount of this action which takes place before the condition of equilibrium is reached; in other words, the surface tension checks that reaction which is accompanied by an increase in that part of the energy of the system which depends upon surface tension. For illustration of the effect of surface tension on chemical action *v. Proc. Camb. Phil. Soc.* 1888. The same principle will show that if the coefficient of compressibility of the solution alters as chemical action proceeds, the amount of this action which takes place before equilibrium is reached will depend upon the pressure applied to the solution; since, if pressure is applied to the liquid, the energy of the system, and therefore its directrix, will alter as the chemical change proceeds. Again, if the coefficient of magnetisation alters as chemical combination goes on, the point at which equilibrium will be reached will depend upon the intensity of the magnetic field in which the solution is placed.

In fine, if the quantity of any kind of energy changes as chemical combination proceeds, the conditions for chemical equilibrium will depend on the amount of the energy possessed by the system.

The amount of the alteration in the value of κ, the value of $\frac{\zeta^c\epsilon^d}{\xi^a\eta^b}$ produced by an alteration χ in the directrix, is given by the equation

$$\frac{\delta\kappa}{\kappa} = -\frac{a}{R_1\theta}\,\frac{d\chi}{d\xi}.$$

If we apply dynamical methods to heterogeneous systems we shall get exactly the same equations as those we previously deduced from kinematical principles. J. J. T.

EQUINIC ACID. A crystalline acid said to exist in fresh mare's-milk (Duval, *C. R.* 82, 419).

EQUISETIC ACID *v.* Aconitic acid.

EQUIVALENCY. The conception of chemical equivalence is founded upon the relations between acids and bases. In the latter part of the last century some interesting and important investigations were carried on by Bergmann, Kirwan, Wenzel, and Richter on neutralisation. Their object was to determine the relative quantities of acids and bases which are necessary to effect neutralisation. Taking a certain quantity of an acid, they attempted to determine the quantities of various bases which were necessary to neutralise this quantity of the acid; and on the other hand, taking a certain quantity of a base, they attempted to determine the quantities of various acids necessary to neutralise this quantity of the base. The important result was reached that there is a simple relation between the quantities of bases necessary to neutralise a definite quantity of an acid, and the quantities of acids necessary to neutralise a definite quantity of a base. Not long after this discovery was made, the fact that the elements combine according to a similar law, called the law of definite proportions, was discovered. This discovery, and that of the law of multiple proportions, suggested at once an enlargement of the old atomic hypothesis, and the connexion between the relative weights of the elements which enter into combination and the relative weights of the atoms was pointed out. Owing to serious difficulties in the way of determining the atomic weights, some chemists felt the necessity of getting back upon a more solid foundation than was afforded by the atomic theory in the form which it then had. It was proposed to give up the hypothesis in dealing with the proportions by weight in which the elements combine; and it was at this time that Wollaston introduced into chemistry the word equivalent. Wollaston proposed to do for the elements what some of his predecessors had done for the acids and bases. He proposed to determine the relations between the weights of the elements which combine with one another, and then to state these relations without reference to any hypothesis. The figures expressing these relations he proposed to call equivalents. The meaning of the word is simple enough. When the statement is made that 35·5 parts of chlorine are equivalent to 80 parts of bromine and 127 parts of iodine, the meaning is only that 35·5 parts of chlorine, 80 parts of bromine, and 127 parts of iodine combine with exactly the same number of parts of some other element, as, for example, with 1 part of hydrogen, 23 parts of sodium, 39·1 parts of potassium, &c. &c. The quantities named of chlorine, bromine, and iodine, are equivalent in their combining power. Clearly, figures determined in this way are independent of hypothesis.

Turning back to the acids and bases, it will be seen that the problem with which Bergmann, Richter, and others were engaged was of the same general character. In their neutralisation experiments they determined the equivalents of the acids and bases. They determined how much of a given acid is necessary to neutralise a certain quantity of a base, and how much of a second acid is necessary to neutralise the same quantity of the same base; and the quantity of the first acid was equivalent to the quantity of the second acid. So also the equivalents of the bases could be determined. Thus it is clear that the equivalent quantities of all acids on the one hand, and the equivalent quantities of all bases on the other, might be determined. By enlarging the meaning of the word equivalent, a given quantity of a base and the quantity of an acid which it can neutralise might be called equivalent.

On first thought, it would appear to be a simple matter to determine the equivalents of acids and bases; but difficulties are soon met with. We can easily determine the equivalent quantities of hydrochloric, hydrobromic, and hydriodic acids, and as each of these acids forms but one salt with a simple base, like caustic potash, the results obtained leave us in no doubt. When, however, we attempt to determine the quantity of sulphuric acid which is equivalent to 36·5 parts of hydrochloric acid, we find that the acid forms two salts with such a base as caustic potash. If we take one of these as the guide the equivalent of the acid will be one number; if we take the other salt as the guide the equivalent will be entirely different. It may be said that one of these salts has an acid reaction, and therefore, as it is obviously not neutral, it should not be taken as the guide. But if we take the case of phosphoric acid, we shall easily be misled if we depend upon the reactions of the salts to inform us which one should be used in determining the equivalent of the acid. This acid forms three salts with caustic soda. The quantities of the base necessary to form these salts are to one another as 1 to 2 to 3. As is well known, only the second salt has a neutral reaction, the third one being distinctly alkaline, and the first one acid. Why not then agree to measure the equivalents of the acids by means of those salts of the acids which contain the largest proportion of the basic constituent? That would lead us into another difficulty due to the fact that some bases have the power to form what are called basic salts, and others have not. Should we determine the equivalent of an acid by means of a base which forms basic salts, we should get one result, while if we should determine the equivalent by means of a base which does not form basic salts we should get quite a different result. Similar difficulties are encountered in attempting to determine the equivalents of the bases.

The determination of the equivalents of chlorine, bromine, and iodine is easily made. Each of these elements combines with hydrogen in only one proportion. As hydrogen has the smallest equivalent, the idea suggests itself at once of using this element as the measure of the equivalents of all the other elements. The problem would then be simply to determine the quantities of other elements which enter into combination with a fixed quantity of hydrogen, and the figures representing these quantities would bear to one another the relations of the equivalents. Using this method, it is found that the equivalent of sulphur is 16, that of nitrogen 4⅔, that of oxygen 8, &c.

The case of carbon presents peculiar difficulties, for the reason that this element combines with hydrogen in a great many different proportions. In one of the compounds 1 part of hydrogen is combined with 3 parts of carbon, in another with 4 parts, in another with 4½ parts, in another with 6 parts, &c.

But most of the elements do not combine with hydrogen. In these cases how shall we determine the equivalents? It seems to be fair to use some other element, as, for example, chlorine, the equivalent of which has been determined by means of the hydrogen standard. As 35·5 parts of chlorine are equivalent to 1 part of hydrogen, it is only necessary to determine what weight of some other element combines with 35·5 parts of chlorine in order to know the equivalent of this other element. Thus 39·1 parts of potassium, 23 parts of sodium, 20 parts of calcium, and 9 parts of aluminium, combine with 35·5 parts of chlorine, and, therefore, the figures just given represent the equivalents of these elements. If chlorine is used as a measure of equivalence, then in some cases results are obtained which are different from those obtained when hydrogen is used as the measure. Thus the equivalent of phosphorus measured by hydrogen is 10⅓, whereas measured by chlorine it is either 10⅓ or 6⅕. We may, however, agree to measure by means of chlorine the equivalents of only those elements which do not combine with hydrogen, though it would be hard to give any reason for this, except that we are led into difficulties unless the use of chlorine is thus limited. Does this end the difficulties? By no means. Iron combines with chlorine in two proportions. In one of the compounds 14 parts of iron, in the other only 9⅔ parts of iron, are combined with 35·5 parts of chlorine. What is the equivalent of iron? If we agree to regard 14 parts of iron as equivalent to 35·5 parts of chlorine, in what light shall we regard the 9⅔ parts which, in the other chloride, also hold in combination 35·5 parts of chlorine? Are these also equivalent to 35·5 parts of chlorine? If so, then plainly we are led to the startling conclusion that 14 parts of iron are equivalent to 9⅔ parts of iron.

It appears that any attempt to determine the equivalents of the elements without reference to some hypothesis must end in failure, or at least it must lead to unsatisfactory results. There is so much room for doubt in regard to which figure to select as the equivalent that, in many cases, two, and even more than two, equivalents might with equal right be selected by different investigators. Plainly, the solid foundation which Wollaston desired, and which we all desire, is not furnished by a system of equivalents. In dealing with similar elements and similar compounds we can speak of equivalent quantities without danger of confusion. Thus, for example, we cannot be misunderstood in speaking of equivalent quantities of chlorine, bromine, and iodine; of nitric acid and hydrochloric acid; of sulphuric acid and sulphurous acid. At present, however, the word equivalent is used very much less than it was in the early part of this century, for the reason that other and clearer conceptions have been introduced into the science. What relation the equivalent bears to the later conceptions will be shown further on.

For the cases named above, and for similar cases in which an element combines with another in more than one proportion, it may be assumed that in one compound a certain number of equivalents of the one element are in combination with one equivalent of the other element, while in the second compound another number of equivalents of the second element are in combination. Thus, in water, 8 parts of oxygen are in combination with 1 part of hydrogen, while in hydrogen dioxide 16 parts of oxygen are in combination with 1 part of hydrogen. It may be assumed that in water one equivalent of oxygen is combined with 1 equivalent of hydrogen, while in hydrogen dioxide 2 equivalents of oxygen are in combination with 1 equivalent of hydrogen. In this case, what is an equivalent? How can we properly speak of 2 equivalents of one element combining with 1 equivalent of another? In doing so we unconsciously make use of an hypothesis, and, if we attempt to express this hypothesis in words clearly, we shall certainly find that it is essentially the atomic hypothesis of Dalton, according to which the combination of elements takes place between small particles which have definite weights. Call these weights equivalents, combining weights, or atomic weights, the hypothesis is essentially the same. The moment we accept such an hypothesis the problem of determining equivalents in the new sense becomes the determination of the relative weights of the smallest particles of the elements which enter into chemical combination. To these new weights the term equivalent is not applicable. It may, however, be retained in its old sense, while the name atomic or combining weight is applied to the smallest weight of an element which enters into chemical combination. This atomic weight may or may not be identical with the equivalent.

To make this clear we may consider the case of nitrogen. As we have seen, the equivalent of nitrogen, deduced from a consideration of the composition of ammonia, is $4\frac{2}{3}$. On studying the compounds of nitrogen carefully we soon find that the quantity of nitrogen found in these is generally considerably larger than is represented by the figure $4\frac{2}{3}$. Thus in nitric acid to 1 part of hydrogen there are 14 $(=3 \times 4\frac{2}{3})$ parts of nitrogen; and when ammonia enters into combination with other substances, as with hydrochloric and nitric acids, the quantity which thus combines is three times as great as that which is represented by one equivalent ($4\frac{2}{3}$ parts) of nitrogen and one equivalent (1 part) of hydrogen. Or, instead of $5\frac{2}{3}$ parts of ammonia being the smallest weight of the substance which enters into combination, this smallest weight is 3 times $5\frac{2}{3}$ parts or 17 parts. When ammonia acts upon hydrochloric acid, for example, 36·5 parts of the acid combine with 17 parts of ammonia, and not with $5\frac{2}{3}$ parts. Similar observations are made in the cases of all compounds of ammonia. Further, a study of certain changes which can be effected in ammonia shows clearly that the hydrogen contained in the substance can be taken out one-third at a time in three stages, and other things put in its place, thus proving that in the smallest particle of ammonia there must be contained at least three smallest particles of hydrogen. The nitrogen cannot, however, be thus displaced in parts. If it leaves the compound at all, all of it leaves at once. Taking, then, all our knowledge together, it appears that the smallest particle of nitrogen which enters into chemical combination is 14 times heavier than the smallest particle of hydrogen, and that in ammonia one of these particles of nitrogen is in combination with three of the smallest particles of hydrogen. We therefore call 14 the combining weight, or, now, accepting the hypothesis, the atomic weight, of nitrogen. But the equivalent of nitrogen is not changed by this; the equivalent remains $4\frac{2}{3}$. The atomic weight is three times as great as the equivalent.

The case of carbon is also instructive. Taking marsh gas it appears that the equivalent of carbon is 3, as in this compound 3 parts of carbon are combined with 1 part of hydrogen. But the hydrogen of marsh gas can be easily displaced by other elements, and four distinct steps in the reaction can be recognised. In each step one-fourth of the hydrogen is displaced. In all the reactions of marsh gas a quantity takes part which contains 12 parts of carbon and 4 parts of hydrogen. Further, an extensive study of carbon compounds has shown that the smallest particle of this element which enters into chemical action is twelve times as great as the smallest particle of hydrogen found in combination. Therefore, we say the atomic weight of carbon is 12. But the equivalent of carbon as deduced from the analysis of marsh gas is 3. The atomic weight is four times as great as the equivalent. Similar studies of oxygen compounds have shown that the atomic weight of oxygen is 16, while its equivalent is 8, or the ratio of equivalent to the atomic weight is 1:2 On the other hand, the atomic weights of chlorine, bromine, and iodine are 35·5, 80, and 127 respectively, and these are also the equivalents; so that while, in the case of carbon, the ratio of the equivalent to the atomic weight is 1:4, in the case of nitrogen 1:3, and in the case of oxygen 1:2; in that of chlorine, bromine, and iodine it is 1:1. This suggests that there is some fundamental difference between chlorine, oxygen, nitrogen, and carbon, which is not taken into consideration in the atomic hypothesis of Dalton. Study of other elements besides those mentioned shows that they may be divided into classes according to the ratio between the equivalent and the atomic weight. This ratio varies from 1:1 to 1:6.

It has already been pointed out that the determination of the equivalents of the elements is a difficult problem. The determination of atomic weights by chemical means alone is also a difficult matter. Although by analysing chemical compounds and studying the chemical changes which these compounds undergo, we can draw conclusions as to the atomic weights of some of the elements, yet as to others we should be left in doubt if assistance were not furnished by a study of some of the physical properties of the compounds. In the article on ATOMIC AND MOLECULAR WEIGHTS (vol. i. p. 336) the application of Avogadro's hypothesis, and of the law of Dulong and Petit regarding the specific heat of the elements, to the problem of determining atomic weights, has been discussed. It is an important fact that the atomic weights determined by the physical methods are in most cases those which experience has shown to be best adapted to the interpretation of known chemical reactions. Not only does Avogadro's hypothesis give us a method for determining atomic weights, but primarily it leads us to definite values for molecular weights. By determining the molecular weights and analysing the compounds, and thus determining the atomic weights, we are led to definite conceptions regarding the composition of the molecules of compounds and of elements. At present we endeavour to express the composition of molecules by our formulæ.

There are now three conceptions to be distinguished carefully from one another. These are the *molecule*, the *atom*, and the *equivalent*. By the molecule is meant the smallest gaseous particle of a substance, whether elementary or compound, which exhibits the characteristic properties of the substance; by the atom is meant the smallest particle of an element which enters into the composition of molecules. The basis upon which the conceptions of molecule and atom rest is considered more fully in the article on ATOMIC AND MOLECULAR WEIGHTS.

With these conceptions clearly in mind we may now ask, what is the equivalent of an element? It is that mass of the element which combines with one atom of hydrogen. In the case of oxygen it corresponds to half the atom, in that of nitrogen to one-third the atom, and in that of carbon to one-fourth the atom. With those elements which do not combine with hydrogen some other element like hydrogen in respect to the ratio between the equivalent and atomic weight is taken as the measure of the equivalent. The results reached in this way have already been referred to.

While those investigations were in progress which finally led to the clear recognition of the difference between atoms and molecules, chemists came to recognise resemblances between different classes of compounds, and it was finally suggested that all compounds are related to a few simple ones, which may be regarded as types. For example, hydrochloric acid, HCl, hydrobromic acid, HBr, and hydriodic acid, HI, are similar compounds and they have a similar composition. Of such compounds, hydrochloric acid, HCl, may be taken as the type. Water H_2O, hydrogen sulphide H_2S, and other compounds belong to the water type. Ammonia NH_3, phosphine PH_3, arsine AsH_3, belong to the ammonia type. Marsh gas CH_4, silicon hydride SiH_4, belong to the marsh-gas type. This classification of compounds according to the type was extended so as to include most compounds, even those which are complex. Serious difficulties were met with in many cases. In some, the difficulty was due mainly to the fact that one and the same compound could belong at the same time to two or more types. This led to the introduction of mixed types. In other cases the difficulty was due to the fact that the reactions of the substance gave little or no clue to its type. In such cases the imagination was freely brought into play with highly unsatisfactory results. Notwithstanding the difficulties which were encountered in the attempt to classify compounds according to types, the attempt led to valuable results. It led to a clearer recognition of differences between molecules, differences which are as real as the molecules themselves. The recognition of these differences does not, however, carry with it any explanation. For to say that each of these compounds belongs to a certain type is not even to attempt an explanation. It is simply the statement of what appears to be a fact. We might determine with certainty to which type or types every known chemical compound belongs, and yet be no nearer an understanding of the differences between the compounds than before the determination. This was first clearly seen by Kekulé, who showed that, in order to understand the relations which exist between the various chemical compounds, it is necessary to go back to the atoms themselves, and inquire what relations they bear to one another in the molecules. The cause of the difference between hydrochloric acid, water, ammonia, and marsh gas, is to be looked for in the atoms of chlorine, oxygen, nitrogen, and carbon. Obviously the first conclusion that forces itself upon us is that the atoms of different elements differ with respect to the number of hydrogen atoms with which they can combine to form compound molecules. While one atom of chlorine combines with only one atom of hydrogen, one atom of oxygen combines with two atoms of hydrogen, one atom of nitrogen combines with three atoms of hydrogen, and one atom of carbon combines with four atoms of hydrogen. Having recognised this difference, the question suggests itself whether an atom of chlorine can hold more than one atom of hydrogen in combination; further, whether an atom of oxygen can combine with a larger or smaller number of hydrogen atoms than two; and similar questions arise with reference to nitrogen and carbon. How far, in other words, are the differences which we have observed fixed and invariable? These questions can be answered only by carefully studying the compounds of the elements named. There is only one compound of hydrogen and chlorine. It therefore appears that one atom of chlorine can hold but one atom of hydrogen in combination, and similarly one atom of hydrogen can hold but one atom of chlorine in combination. Oxygen and hydrogen, however, combine in two different proportions forming the compounds H_2O and H_2O_2; while in water it appears that one atom of oxygen holds two atoms of hydrogen in combination, in hydrogen dioxide it appears that two atoms of oxygen hold two atoms of hydrogen.[1] Nitrogen and hydrogen form but one compound with each other. Carbon and hydrogen on the other hand form a large number of compounds with each other. Of these only one contains a single atom of carbon in the molecule. That is marsh gas, and in the molecule of this compound there are four hydrogen atoms to the atom of carbon. There are three compounds of these elements in whose molecules there are two atoms of carbon. They are C_2H_6, C_2H_4, and C_2H_2. Before attempting to explain this let us see what general conclusion is justified by the facts above recorded. What is true of the relations of chlorine and hydrogen is equally true of bromine and hydrogen, and of iodine and hydrogen. What is true of oxygen and hydrogen is true of sulphur, selenion, and tellurium, and hydrogen. What is true of nitrogen and hydrogen is true of phosphorus, arsenic, and antimony, and hydrogen. And, finally, what is true of carbon and hydrogen, so far as their relations in marsh gas are concerned, is also true of silicon and hydrogen. We are therefore justified in making the statement that the atoms of different elements differ from one another with reference to the number of atoms of hydrogen they can combine with to form compound molecules. As regards formation of molecules, the atoms of the elements can be divided into at least four classes:—

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[1] But it is to be observed that as hydrogen peroxide has not been gasified, the formula H_2O_2 does not necessarily represent the atomic composition of the molecule of this compound.—M. M. P. M.

1. Those which combine with hydrogen in the simplest proportion of one atom to one atom of hydrogen.

2. Those which combine with hydrogen in the proportion of one atom to two atoms of hydrogen.

3. Those which combine with hydrogen in the proportion of one atom to three atoms of hydrogen; and

4. Those which combine with hydrogen in the proportion of one atom to four atoms of hydrogen.

Our conception of the chemical atom is thus enlarged. It is not only a minute particle of matter, which in chemical changes is not broken up, and which has a definite mass, and the power of combining with other atoms, but it also has some power which determines how many atoms of another kind it can combine with. At present we cannot form a clear conception as to the cause of this power, and no hypothesis has as yet been proposed to account for it. We can represent the fact by means of symbols, but these symbols do not help us to understand the cause, though they are convenient. We may also adopt figurative forms of expression suggested by our symbols, but this has not as yet advanced our knowledge of the cause of the property of the atoms with which we are dealing.

On examining the composition of the molecules of the compounds which any element forms with other elements than hydrogen, we find that just as the number of hydrogen atoms with which one atom of the element can combine is limited so the number of atoms of other elements with which it can combine is limited. Thus phosphorus combines with chlorine to form the compounds PCl_3 and PCl_5, with hydrogen to form the compounds PH_3 and P_2H_4, and with oxygen to form the compounds P_2O_3 and P_2O_5. Sulphur combines with hydrogen to form the compounds SH_2 and probably S_2H_2, with chlorine to form the compounds S_2Cl_2, SCl_2 and SCl_4, and with oxygen to form SO_2 and SO_3, *&c.*, *&c.* From facts like these we conclude *that atoms are so constructed, or act in such ways, that the number of other atoms with which each can combine is limited, and that as regards the number of other atoms with which they can combine, they differ from one another.*

The property of an atom which determines the number of other atoms with which it can combine to form a compound molecule is called its *valency.* The relation between the atomic weight of an element, its equivalent, and its valency, will readily be understood by the aid of a few examples. The atomic weight of nitrogen, as determined by chemical and physical methods, is 14; its hydrogen-equivalent is $4\frac{2}{3}$, as this is the relative weight of nitrogen which combines with one part by weight of hydrogen. The number of atoms of hydrogen with which the atom of nitrogen combines is 3 or $\frac{14\text{ (at. wt.)}}{4\frac{2}{3}\text{ (equiv.)}}$. So also in the case of carbon. The atomic weight of carbon is 12, its hydrogen-equivalent is 3; the number of hydrogen atoms with which an atom of carbon can combine is $\frac{12\text{ (at. wt.)}}{3\text{ (equiv.)}} = 4$, *&c.* In general, the number of hydrogen atoms with which the atom of any element can combine is expressed by a figure which also expresses the relation between the atomic weight and the hydrogen equivalent of the element.

The recognition of the property called valency proved of the highest importance for chemistry. Discussions in regard to this property have now been carried on for nearly thirty years, and our views in regard to the structure of chemical compounds are based upon it. It is, therefore, desirable to study it with some care, with the object of determining exactly what is known in regard to it, so that we may be in a position, on the one hand, to recognise its value, and, on the other hand, to avoid the dangers to which we are exposed in following the conception blindly.

Before the introduction of the conception of valency, each chemical compound was looked upon as a whole. To be sure, the difference between atoms and molecules, first pointed out by Avogadro, gradually came to be recognised, and in a general way it was acknowledged that the molecule is made up of atoms. But, beyond this, inquiry was not pushed to any extent. This is shown in an instructive way by a study of the investigations of Hofmann, Wurtz, and others, on the so-called substituted ammonias. When Hofmann began his investigations on aniline, the prevailing view in regard to this compound was that it was a conjugated compound (*gepaarte Verbindung*); that it contained ammonia combined with a hydrocarbon. Using the modern atomic weights, the view referred to is expressed by the formula $C_6H_4.NH_3$. The common reactions of aniline were interpreted by supposing that the group C_6H_4 simply accompanied the ammonia. Some time before this Liebig had suggested that certain bases like aniline might be regarded as containing the group NH_2. According to this 'amide theory' of Liebig, aniline is to be represented by the formula $C_6H_5.NH_2$. In this compound, then, ammonia as such is not supposed to be present, but, nevertheless, there is in it a remnant of ammonia which gives to the compound certain of the characteristic properties of ammonia. Wurtz discovered the bases methyl-amine and ethyl-amine at the time that Hofmann was engaged in his studies on aniline, and at about the same time each suggested that the substances he was working with might be regarded as ammonia in which one of the hydrogen atoms is replaced by a radicle. Before Hofmann closed his work on aniline he furnished strong experimental evidence against the theory of conjugated compounds as far at least as it applies to aniline. He showed that the reactions between ammonium oxalate and phosphoric anhydride are not the same as those between aniline oxalate and phosphoric anhydride, and that the difference cannot be understood if aniline be regarded as a conjugated compound, but that it is easily explained if aniline be regarded as ammonia in which one hydrogen has been replaced by the hydrocarbon residue C_6H_5. The subsequent preparation of substituted ammonias in which two and three hydrogen atoms of ammonia were replaced by radicles, and of compounds derived from ammonium by the replacement of all the hydrogen atoms, furnished a solid foundation for the view put forward in the so-called theory of types. As has already been stated, according to the theory of types every compound is built according to some plan, and the number of plans according to which compounds are built is small, the fundamental plans or types being hydrogen HH, hydrochloric acid HCl, water H_2O, and ammonia H_3N. Much attention was now given to determining the type to which any given compound belonged, and when, after investigation of the properties and composition of a compound, a definite statement regarding the type to which it belonged could be made, the problem was considered to be solved. No further questions were asked. It was as if one should look alone at the exterior of buildings, and compare them solely with reference to the exterior, without making any inquiry with regard to the interior arrangements, the connexions between the rooms, &c.

Shortly after Hofmann's papers appeared, an important paper by E. Frankland was published (1852). The author had been investigating a new class of compounds containing metals. At the close of the paper, the chemical structure of the compounds is discussed. Attention is called to the fact that when a metal has combined with a hydrocarbon, as in the case of tin ethyl, SnC_4H_5 (using old formulæ), the power of the metal to combine with other elements, as oxygen, is not so great as that of the uncombined metal. While tin alone combines with oxygen in two proportions, forming the compounds SnO and SnO_2, tin-ethyl SnC_4H_5 combines with oxygen in only one proportion, forming the compound SnC_4H_5O, and this compound cannot take up any more oxygen even when boiled with dilute nitric acid. Similar observations were made with reference to the corresponding derivatives of antimony and arsenic. In commenting further upon these remarkable facts, the author shows that they are directly opposed to the theory of conjugated compounds, according to which the compounds under consideration are regarded as containing the unchanged metals conjugated with hydrocarbons. He then says: 'When the formulæ of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction; the compounds of nitrogen, phosphorus, antimony, and arsenic especially exhibit the tendency of these elements to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternal group we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, SbH_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, &c., and in the five-atom group NO_5, NH_4O, NH_4I, PO_5, PH_4I, &c. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms' (*Philosophical Transactions*, 1852, p. 440).

Thus the conception of the saturation of atoms was introduced into chemistry. It was soon taken up by others, as Williamson and Odling, and finally, at about the same time in 1858, Kekulé and Cooper showed how this conception might be applied to the explanation of the constitution of chemical compounds in general. Kekulé took up the problem in a broad way, and it is largely due to his efforts that the conception of valency became the controlling conception in the discussions in regard to the structure of chemical compounds. Kekulé says: 'I consider it necessary, and, in the present condition of chemical knowledge, in many cases possible, in the explanation of the properties of chemical compounds, to go back to the elements themselves which make up the compounds. I do not consider the chief task of investigation to be the detection of groups of atoms which on account of certain properties are to be regarded as radicles, and thus to refer the compounds to a few types which are scarcely more than sample formulæ. I believe rather that investigation may include the radicles themselves, and point out the relations between the radicles, and that, from the nature of the elements, the nature of the radicles and of the compounds can be deduced.'

In the valencies of the atoms we now find the explanation of types. The reason why most compounds are to be compared with hydrochloric acid, water, ammonia, and marsh gas, is that the atoms of most elements are like chlorine, oxygen, nitrogen, or carbon in respect to the number of atoms of other elements with which they can combine. The simplest kind of atom is one like that of chlorine or hydrogen; next come those which are like those of oxygen. The chlorine atom can hold in combination but one atom of hydrogen: the oxygen atom has twice this power, it can hold two atoms of hydrogen in combination; the nitrogen atom can hold three atoms of hydrogen in combination; and finally the carbon atom can hold in combination four atoms of hydrogen. Chlorine, oxygen. nitrogen, and carbon represent these four different kinds of elements.

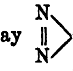
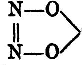
Chlorine is called a *monovalent* element, because its atom combines with but one atom of hydrogen to form a compound molecule; oxygen is called a *divalent* element, nitrogen a *trivalent*, and carbon a *tetravalent*, element. Further, the elements are called respectively *monads*, *dyads*, *triads*, *tetrads*, *pentads*, *hexads*, &c.

From what has been said it will be clear that valency is something quite different from affinity. By affinity is commonly meant the unknown cause of the combination of atoms. Hydrogen and chlorine combine very readily; they have, as we say, a strong affinity for each other; yet they are monovalent with reference to each other. Carbon and chlorine do not combine readily: they have not a strong affinity for each other; yet carbon is tetravalent towards chlorine, its atom is capable of holding four atoms of carbon in combination. The two properties valency and affinity are possessed by every atom, and exhibit themselves whenever atoms act upon one another, the latter determining the intensity of the reaction, the former the complexity of the resulting molecule.

In this discussion thus far the valency of an element has been measured by considering the number of atoms of hydrogen with which its atom can combine to form a compound molecule. It is, however, a fair question whether the valency of an element towards other elements is necessarily the same as towards hydrogen. Is it fair to conclude that, because an element is trivalent towards hydrogen, it is also trivalent towards chlorine and other elements? As we have yet no conception in regard to the cause of the property which we call valency, we have not a right to make assumptions of this kind. The only way to answer the question is to study the facts. For this purpose let us take the case of carbon. This element is tetravalent towards hydrogen. Towards chlorine it is also tetravalent, as is shown by the molecule CCl_4. Towards oxygen it appears to be tetravalent in carbon dioxide, CO_2, in which we have the atom of carbon in combination with two divalent atoms of oxygen. But in carbon monoxide, CO, either carbon acts as a divalent element or oxygen acts as a tetravalent element. Towards sulphur carbon is tetravalent, as shown in carbon disulphide, CS_2, in which one atom of carbon holds in combination two divalent atoms of sulphur. Phosphorus is trivalent towards hydrogen, it cannot form a compound with hydrogen containing a larger number of atoms of hydrogen than three. It is, however, pentavalent towards chlorine, as shown in the compound phosphorus pentachloride, PCl_5, and it is also trivalent towards this element, as shown in the trichloride PCl_3. Phosphorus also combines with oxygen in two proportions, forming the trioxide, P_2O_3, and the pentoxide, P_2O_5, and the compositions of these can be best explained by assuming that, in the former, the phosphorus is trivalent, and, in the latter, pentavalent. Sulphur is divalent towards hydrogen, forming the compound SH_2. With chlorine it forms the compounds S_2Cl_2, SCl_2, and SCl_4. With oxygen it forms the compounds SO_2 and SO_3, in which the sulphur appears to be tetravalent and hexavalent. Iodine is monovalent towards hydrogen, but towards chlorine it acts both as a monovalent and as a trivalent element, as shown in the compounds ICl and ICl_3. Nitrogen, which is only trivalent towards hydrogen, appears to be pentavalent in the compound NH_4Cl and other similar ammonium compounds. With oxygen it combines in a number of proportions, as is well known.[1]

The simplest interpretation of the facts just stated is that the valency of an element towards hydrogen is not necessarily its valency towards other elements, and that the valency of one element towards another may be one thing in one compound and different in another compound. Although this is the *simplest* interpretation, it does not follow that it is the correct one. It is possible that the valency of an element is always the same, but that, owing to the surrounding conditions and the character of the element with which it combines, the full valency is not always exhibited. Until we have a clear conception in regard to the cause of valency, or until we have a satisfactory hypothesis of valency, discussions on the question whether valency is constant or variable must be more or less idle. If valency be something inherent in the atom, like the mass of the atom, then it is impossible to conceive of it as being variable. If, however, it be a condition of the atom; if, for example, it is dependent on the motion of the atom, then, as the motion may differ under different circumstances, the valency also may differ.

It is not uncommon to think of atoms as joined together in some such way as small objects adhere to one another under the influence of electric or magnetic attraction. It is supposed that the monovalent atom has but one place where another atom can be attached, or that it has but one pole, or that there is but one direction in which another atom can enter into combination with it. These phrases do not help us much, and they do not differ materially from one another. If such a view is held, it carries with it, of course, a similar view in regard to divalent, trivalent, and, in general, polyvalent, atoms. Each atom has a number of places where other atoms can be attached, the number corresponding to the valency of the atom. The graphic symbols so commonly used to represent the structure of chemical compounds in terms of the conception of valency are well calculated to give the idea that the view just stated is generally accepted. Of course, if it is accepted, valency is considered as a constant property. In this case it will be necessary to furnish explanations of those compounds which seem to prove that valency is variable. Some of the explanations which have been offered will now be considered.

Among the compounds which appear to show that valency is variable is the well-known series of oxygen compounds of chlorine and of nitrogen. While chlorine forms only one compound with hydrogen, and is unquestionably monovalent towards hydrogen, it appears to have a greater valency towards oxygen. This is explained by some by assuming that in those compounds of chlorine and oxygen in which there is more than one atom of oxygen in the molecule the oxygen atoms are combined with each other as represented in the formulæ Cl—O—O—Cl and Cl—O—O—O—Cl, in which the chlorine is represented as monovalent and the oxygen as divalent. To explain the existence of the series of oxides of nitrogen, on the assumption that the valency of oxygen is always two and that of nitrogen three, a similar method is used; if necessary, combination is assumed between nitrogen atoms, between oxygen atoms, and between nitrogen and oxygen atoms. But even with these possibilities all these compounds cannot be explained without the aid of a new conception. It is assumed that a polyvalent element may be in combination with itself in more than one way. Just as hydrogen in the hydrogen molecule must be assumed to be in combination with itself in the same way that it is in combination with chlorine in the molecule of hydrochloric acid, so oxygen must be in combination with itself in the molecule of oxygen. But oxygen is divalent; *i.e.*, on the present hypothesis, its atom has two places where combination with other atoms can be effected. To express the conception that both these places are occupied in the molecule of oxygen, this molecule is represented graphically thus O=O, while the molecule of hydrogen is represented thus H—H. The latter condition is spoken of as single union, the former as double union. So, too, triple union is supposed to exist in the molecule of nitrogen as represented thus N≡N. Now, in explaining the oxides of nitrogen it is assumed that in some cases the nitrogen atoms are in combination by single union, and in others by double union. Thus nitrous oxide N_2O is represented in this way ; the trioxide thus . The compounds NO and NO_2 plainly cannot be explained in this way. For these a new assumption, which will be considered later, must be made. The tetroxide N_2O_4 may be represented in this way $\begin{array}{l} N-O-O \\ \| \qquad\quad | \\ N-O-O \end{array}$.

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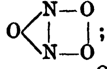
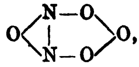
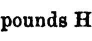
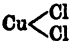
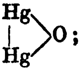
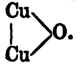
[1] It is important to note that many of the compounds cited above have not been gasified, and that therefore the formulæ given are not all molecular; it is known that some of the compounds, *e.g* PCl_5 and NH_4Cl, are dissociated by heat. It is doubtful whether arguments regarding the valencies of atoms should be based on the compositions of any compounds except those which have been gasified; as it is only to gases that the conception of the theory of atoms and molecules can, at present, be strictly applied.—M. M. P. M.

The question will now suggest itself, have we any evidence that the structural formulæ above given are correct? Is there any experimental evidence in favour of them? The answer is that we have no evidence whatever in favour of them, and the only reason for accepting them is that they are in accordance with the indefinite and crude view in regard to the nature of valency above referred to. The argument is this: valency must be a constant property of elementary atoms; but nitrogen is trivalent and oxygen is divalent; therefore the compounds of these elements must be constituted in the way represented. It must, however, be distinctly borne in mind that for some of the compounds there are other formulæ, besides those given above, which answer the requirements, and which are just as probable. For example, nitrogen trioxide may be represented thus ; and the tetroxide thus , or thus $\begin{array}{l} O-N-O \\ | \qquad | \qquad | \\ O-N-O \end{array}$.

In explaining the existence of the two series of compounds of mercury, copper, iron, aluminium, &c., the same method is commonly adopted. Mercury and copper are regarded as divalent in both series of compounds, and the structure of the compounds is represented thus: mercuric compounds , Hg=O; cupric compounds  and Cu=O; mercurous compounds $\begin{array}{l} Hg-Cl \\ | \\ Hg-Cl \end{array}$, ; cuprous compounds $\begin{array}{l} Cu-Cl \\ | \\ Cu-Cl \end{array}$ and .

There are many cases which cannot be explained by any of the assumptions thus far referred to. As good an example as any is that of the two chlorides of phosphorus, PCl_3 and PCl_5. Here, plainly, phosphorus is in combination with chlorine in more than one proportion, and this cannot be explained by assuming that in one of these compounds two atoms of phosphorus are in combination with each other, for the molecular weights of the chlorides are properly represented by the above formulæ. It has been suggested by Kekulé that the pentachloride is not a true chemical compound, but that it is made up of a molecule of phosphorus trichloride and a molecule of chlorine held in combination by some force different in character from that which holds the atoms together in a molecule. This conception may be represented thus $PCl_3.Cl_2$. The fact that when the compound is heated it readily breaks down, forming the trichloride and free chlorine, was regarded by Kekulé as evidence in favour of the view which he put forward. He called compounds of this kind 'molecular compounds,' to distinguish them from true chemical compounds or atomic compounds. He considered them to be similar to salts with water of crystallisation, from which the water is given off by heat.

One serious objection to this view is that many of the cases which it was invented to explain cannot be explained by it. While it is true that phosphorus pentachloride does break down under the influence of heat, the analogous pentafluoride is stable, and there is no reason for assuming that it differs from other chemical compounds. Then, too, it has been shown that the pentachloride itself can be converted into vapour in the presence of the vapour of the trichloride. At present this hypothesis of molecular compounds does not play an important part in dealing with the subject of valency.[1]

A more satisfactory suggestion which has been made with reference to the variations in valency is that while an atom may have a constant maximum valency, its entire valency may not be exhibited in certain compounds. Those compounds of an element in which its full valency is brought into play are called *saturated compounds*, and those in which the full effect of the valency is not shown are called *unsaturated compounds*. Thus, according to this view, phosphorus is pentavalent, and in the pentachloride, which is a saturated compound, its full valency is brought into play, while in the trichloride only a part of its valency is brought into play, the compound being unsaturated. The difference between carbon monoxide CO and the dioxide CO_2 is accounted for in the same way. The expressions 'its full valency is brought into play' and 'only a part of its valency is brought into play' cannot at present be further explained, but this is not a sufficient reason for refusing to use them. The facts show clearly that the manifestation of that power which we call valency is subject to variations. We must use some expressions to state these facts. The chief objection to the expressions is that they suggest the idea of parts of an atom acting differently, or of some parts of an atom being brought into action while other parts are not acting, an idea which is not only improbable, but absurd. But this idea is not necessarily involved in the conception of saturated and unsaturated atoms. Thus carbon has the power to combine with oxygen in the proportions indicated by the formulæ CO and CO_2. It is certain that the carbon atom in the monoxide has the power to take up more oxygen, and that when more oxygen is presented to it under the right conditions the additional oxygen is taken up. Because the monoxide can take up as much oxygen as it already contains, it does not follow that the carbon atom in the monoxide is only half employed, any more than it follows that, because a magnet which can support two pounds is supporting only one pound, it is therefore only half employed. The whole magnet acts in both cases: in the one case it is saturated, in the other it is unsaturated. There is, however, this marked difference between the case of the magnet and that of the atom. In the former any weight, from the lightest to that necessary for saturation, can be held in combination, whereas in the latter the variations are determined by the weights of the atoms which are held in combination. Although then it is most probable that in every chemical compound, whether saturated or unsaturated, every atom is brought into action in every part, it appears probable that the atoms can adjust themselves in different ways with reference to one another.

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[1] This is especially true if we agree to restrict our conceptions of valency to the consideration of gaseous molecules.—M. M. P. M.

Some investigations have been undertaken with the object of throwing light upon the question whether different parts of an atom can act differently. To illustrate the methods the case of carbon may be taken. The carbon atom is tetravalent. It combines with four atoms of hydrogen, chlorine, &c., to form compound molecules. Are all the four atoms which it holds in combination held with the same force? The facts appear to give an affirmative answer. If the atoms were held in different ways, then it should be possible to make more than one compound of the formula CH_3Cl, or any other mono-substitution product of marsh gas. But, as a matter of fact, only one variety of these mono-substitution products has ever been prepared. Then, further, the theory in regard to the structure of the hydrocarbons of the paraffin series is based upon the assumption that each of the four hydrogen atoms in marsh gas is held in exactly the same way by the carbon atom; and this assumption is so perfectly in accordance with a large number of facts that it is worthy of the most serious consideration as an argument. There is one experiment which appears to show that in the case of sulphur the four affinities, as the hypothetical individual points of attraction, or the parts into which the total valency may be divided, are called, are not exactly the same. Krüger asserts that the product of the combination of $(C_2H_5)_2S$ and CH_3I is different from the product formed by combining $S(CH_3)(C_2H_5)$ with C_2H_5I; yet both compounds are represented by the formula SEt_2MeI. If it is assumed that in these compounds the sulphur is tetravalent, then it appears to follow that the four affinities of the sulphur atom are not identical in value; because if it were immaterial in what way the groups Et and Me, and the atom I, were arranged relatively to the S atom with which all are in direct union, then only one compound SEt_2MeI could exist.[1] A similar conclusion seems to be justified in the case of nitrogen, as shown by Lossen's investigations on derivatives of hydroxylamine. Lossen showed that when two different radicles are introduced into hydroxylamine in place of hydrogen, a large number of isomeric substances are obtained instead of one, as we should expect. The case of nitrogen has been investigated by V. Meyer and by Ladenburg, but the results obtained by these two investigators differ. Taking all the evidence into consideration it appears that by far the larger number of facts of chemistry clearly indicate that the affinities of an atom are of the same kind, while in the case of sulphur and of nitrogen the facts referred to require further investigation.

It is sometimes held that, because a certain number of atoms are readily given off from a molecule of a compound, there are weaker and stronger affinities. Thus, when phosphorus pentachloride is heated it gives up two atoms of chlorine. From this the conclusion is sometimes drawn that in phosphorus pentachloride three of the atoms of chlorine are held in combination more firmly than the other two. Such a conclusion is, however, evidently unjustified. All that we can say is, that at the higher temperature the more complex compound cannot exist, while the trichloride can. It is probable that in the trichloride the whole of the phosphorus atom is employed in holding the three chlorine atoms in combination, and that this is also true of the phosphorus atom and the five chlorine atoms in the pentachloride. If this is true, then it follows that the pentachloride must be a less stable compound than the trichloride.

Whatever method of explaining the variations in the composition of the compounds of any elements we may adopt, it is plain that these variations are observed. Whether we agree to say that carbon is divalent in carbon monoxide and tetravalent in carbon dioxide, or to call carbon dioxide a saturated compound and the monoxide an unsaturated compound, the facts remain the same; and the most important thing to be done is to discover the laws which express the variations in composition. This subject has received considerable attention, but a law which shall express all cases has not been deduced. Nevertheless a fact of great importance has been learned. It is this, that the apparent valency of an element in nearly all cases changes from even to even or from odd to odd, and but rarely from odd to even or *vice versâ*. Thus the valency of phosphorus changes from three to five, and all compounds of phosphorus can be explained by assuming that the element is either trivalent or pentavalent, and there are no facts known which indicate that it is ever divalent or tetravalent. Sulphur, on the other hand, is apparently divalent in hydrogen sulphide, SH_2, tetravalent in sulphur dioxide, SO_2, and in the tetrachloride, SCl_4, and hexavalent in sulphur trioxide, SO_3; and there is no compound of sulphur requiring the assumption that the element is ever monovalent, trivalent, or pentavalent. Elements whose valencies are expressed by an even number have been called *artiads*, and those whose valencies are expressed by an uneven number have been called *perissads*. Although the division of the elements into *artiads* and *perissads* is justified by many facts, there are a few which show clearly that the law is subject to exceptions. The most prominent of these are the oxides of nitrogen, nitric oxide, NO, and the peroxide, NO_2. Plainly in neither of these is nitrogen trivalent or pentavalent. In the former it appears to be divalent, and in the latter tetravalent, the compounds corresponding in composition to the two oxides of carbon. It is true there is nothing to prevent our regarding the nitrogen as monovalent in nitric oxide, and perhaps representing its structure thus $=N-O-$; but we shall hardly make much progress if we are willing to make use of such methods to deceive ourselves by supposing that we are thus helped out of difficulties; and it should be said, for the credit of chemists, that this suggestion has not been made, so far as is known to the writer.[1]

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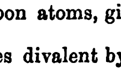
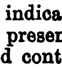
[1] Recent research has invalidated Krüger's results.

The law of variation in the composition of compounds, or in the valency of the elements, is highly suggestive of the law which expresses the variations in what may be called the valency of certain hydrocarbons. The hydrocarbon, C_6H_{14}, is a saturated compound, and is not capable of combining directly with atoms or molecules. In this sense it has no valency, and is to be compared to the elements in the state of molecules. As is well known, the simplest change which can take place in hexane, to convert it into a compound with active valencies, is the abstraction of two atoms of hydrogen. In this way the hydrocarbon, C_6H_{12}, or hexylene, is formed. This compound is divalent. An intermediate monovalent compound cannot be obtained. The next change of the same kind gives a compound, C_6H_{10}, which is tetravalent; and thus successively are formed the hexavalent compound, C_6H_8, and the octovalent compound, C_6H_6. The valencies of these compounds are then 2, 4, 6, and 8, the variations following the same law as is observed in the case of the elements. The variations in the case of the hydrocarbons are commonly explained by assuming different kinds of union between the carbon atoms. The hexavalent group  becomes tetravalent by the establishment of double union between the carbon atoms, giving a group  $C=C$, and it becomes divalent by the establishment of triple union between the carbon atoms as indicated thus, $-C\equiv C-$. Other possibilities present themselves when we have a compound containing more than two atoms of carbon in the molecule. As has already been shown this same method of explanation has been used in the cases of the compounds of mercury, copper, and iron, but it is plainly not directly applicable to the phosphorus compounds, or the sulphur compounds above referred to. It has been suggested by Professor Sylvester (*v. Am.* 1, 54) that the variation in the valency of elements may be accounted for by supposing each *n*-valent atom to be made up of *n*-trivalent atomicules united in such a way as to leave one valency of each atomicule free. The explanation is fanciful, but may perhaps prove of some service.

In studying the valencies of the elements in connexion with their position in the periodic system, certain regularities appear which are of great interest. As regards the hydrogen valency it is a noteworthy fact that the elements of the first three groups in Mendelejeff's table do not unite with hydrogen. Beginning with carbon in the fourth group the hydrogen valency decreases regularly, as is shown in the following table:—

Group	1	2	3	4	5	6	7
Element	Li	Be	B	C	N	O	F
Hydrogen compound	—	—	—	CH_4	NH_3	OH_2	FH

Taking next the chlorine valency we find, beginning with Group 1, a regular increase to Group 4, and then a regular decrease, as is shown in this table:—

Group	1	2	3	4	5	6	7
Element	Na	Mg	Al	Si	P	S	Cl
Chlorine compound	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_2	Cl_2

Towards oxygen the valency increases regularly from Group 1 to Group 7, as shown thus:—

Group	1	2	3	4	5	6	7
Element	Na	Mg	Al	Si	P	S	I
Oxygen compound	Na_2O	Mg_2O_2	Al_2O_3	Si_2O_4	P_2O_5	S_2O_6	I_2O_7

This series of oxygen compounds is of special interest. One cannot study it impartially without reaching the conclusion that we have here to deal with a regular increase in the valency from 1 to 7. Any other conclusion involves an explanation for the compounds P_2O_5, SO_3, and I_2O_7 entirely different from that which we make use of for the other oxygen compounds in the series. Further, when we consider the hydroxyl derivatives of these elements, we shall see that it is impossible to deal with them satisfactorily on any other assumption than that phosphorus is tetravalent, sulphur hexavalent, and iodine heptavalent towards oxygen. This is perhaps most strikingly shown in the case of periodic acid. This compound is commonly represented by the formula HIO_4, and the structure H-O-O-O-O-I is given to it. It can easily be shown, however, that on this assumption most of the salts of periodic acid cannot be explained. Whereas, if the periodates be considered as derived from several acids, all of which are in turn derived from the normal periodic acid $I(OH)_7$ by processes of dehydration, they can all be explained without serious difficulty. The acid HIO_4, according to this, is derived from normal periodic acid thus: $I(OH)_7 = O_3I(OH) + 3H_2O$; and in it the iodine is regarded as heptavalent, holding three atoms of oxygen and one hydroxyl. In a similar way sulphuric acid is regarded as derived from the normal acid or maximum hydroxyl compound $S(OH)_6$ by loss of water:

$$S(OH)_6 = O_2S(OH)_2 + 2H_2O.$$

According to this, in sulphuric acid the sulphur is hexavalent, holding two atoms of oxygen and two hydroxyls. Several facts which have come to light in the study of derivatives of sulphuric acid speak in favour of this view, or at least against the view sometimes held that the acid is constituted thus, HO-O-S-O-OH. In short, whether we study the elements with reference to their positions in the periodic system or with reference to the chemical transformations of their compounds, we are led to the conclusion that the more probable view in regard to their valency towards oxygen is that it increases regularly from 1 to 7 from Group I. to Group VII.; and that the valency of the elements towards hydrogen is quite different from their valency towards oxygen, except in Group N. Taking the last four groups it is seen that as the valency towards hydrogen decreases the valency towards oxygen increases:

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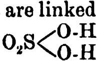
[1] There are several exceptions to the so-called law of *artiads* and *perissads*; $InCl_2$ and $InCl_3$, and probably also InCl, exist as gases; WCl_5 and WCl_6; $CrCl_2$ probably exists as a vapour, besides $CrCl_3$; HgCl is probably the molecular formula of calomel, while the composition of the molecule of corrosive sublimate is represented by the formula $HgCl_2$.—M. M. P. M.

Group	4	5	6	7
Hydrogen compound	SiH_4	PH_3	SH_2	IH
Oxygen compound	Si_2O_4	P_2O_5	S_2O_6	I_2O_7

It appears from further study that the valency of an element towards hydrogen is constant, while towards chlorine and oxygen it is evident from what has already been said that the valency varies. Except in the fourth group the maximum valency is never exhibited towards hydrogen. Chlorine occupies an intermediate place. In the fourth and fifth groups the valency towards chlorine is the same as towards oxygen. In the sixth group the valency towards hydrogen is two, towards oxygen six, and towards chlorine, as shown by the highest chlorine compound of sulphur, it is four. In the seventh group the valency towards hydrogen is one, and towards oxygen seven, while the highest valency shown towards chlorine by a member of this group is three, as in the compound ICl_3. Towards fluorine, however, the valency of iodine is five, as shown by the compound IF_5.[1]

The facts just referred to show beyond question that the valency of an element is not a constant property, residing as it were in the element, but that it is determined to some extent by external circumstances, and particularly by the character of the element with which an element is brought in contact. We find analogy for this in the conduct of some acids towards bases. Thus, ordinary phosphoric acid is commonly spoken of as a tribasic acid, but its basicity is to some extent dependent upon the character of the base with which it reacts. Strictly speaking it is only dibasic towards sodium hydroxide, while towards most other bases it is tribasic. The intensity of the action of the acid towards sodium hydroxide is greater than towards most other bases, and after the acid has taken up two atoms of sodium its power is nearly exhausted. It can, to be sure, take up a third atom of sodium, but the compound thus formed is very unstable. But it can take up and hold firmly in combination three atoms of silver. Considering the differences in the valency of any element towards other elements, it appears in general that the valency is small towards an element with which it combines with much energy, while it is larger towards an element with which it combines with little energy. This is well illustrated by the compounds of chlorine with hydrogen and with oxygen.

The phenomena studied under the head of valency show clearly that, when atoms combine to form a molecule, they are not merged into one homogeneous mass, but are arranged with a certain definiteness; and the study of the facts of isomerism confirms this view in a striking way. We speak of the atoms as being linked together, and this linking is found to take place according to the laws of valency. By the constitution or structure of a compound is meant the way in which the atoms are linked together. The constitution is expressed by means of a formula which is intended to show—on the basis of certain assumptions, and by the help of several conventions—how the atoms are linked together. Thus the formulæ H-O-H,  $O_2S<\begin{smallmatrix}O\text{-}H\\O\text{-}H\end{smallmatrix}$, &c., are constitutional formulæ. These are determined by methods which will be considered in the article FORMULÆ. It need only be remarked here that they are determined chiefly by studying the reactions of compounds, and the methods by which they are built up from simpler substances. The reactions being known, they are interpreted in terms of the atomic theory and the hypothesis of the linkage of atoms.

To sum up in a few words the chief conclusions which we are justified in drawing in regard to valency:—

The so-called theory of types was the forerunner of the valency hypothesis.

Frankland first recognised the fact that the power of atoms to unite with other atoms is limited to a definite number of other atoms.

Kekulé and Couper elaborated the valency hypothesis, and showed how it may be used to explain chemical compounds.

The facts show plainly that valency is not a constant property of the elements, but that it varies: (1) according to the nature of the uniting elements; (2) according to surrounding circumstances, such as the temperature.

Valency is not to be thought of as determined by a certain number of points of attraction in the atom, but rather as a condition—perhaps a form of motion. Valency is a function of the atomic weights of the elements. I. R.

ERBIUM Er. At. w. 166. Mol. w. unknown as element has not been gasified. Chief lines in emission-spectra: 5826, 5256, 4951 (Cleve, *C. R.* 91, 381).

In 1788 Gadolin, professor at Abo, found a new earth in a mineral from Ytterby in Sweden; the discovery was confirmed by Eckeberg in 1797, and the new earth was called *Yttria*. The examination of yttria from *Gadolinite* (the mineral was thus named after Gadolin) by Berzelius (1819), Mosander (1839 and 1843), and Scheerer (1842), led to the recognition of seven earths in what had been regarded by Gadolin as a homogeneous substance, viz. beryllia, lanthana, ceria, didymia, yttria, erbia, and terbia. Many researches were conducted in the years 1860-1878 on the earths from Gadolinite; some of the results pointed to the non-existence of terbia as a distinct earth, while others made the existence of this body very probable; the investigations of Cleve seem to show that terbia is a definite earth. The substance to which the name of erbia had been given was very carefully examined by Marignac in 1878, and subsequently by Nilson, and then by Cleve, with the result that it was shown to be a mixture of the three earths ytterbia, scandia, and erbia, and to these Cleve afterwards added two others, viz. holmia and thulia. The investigation of these earths is yet far from complete.

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[1] If by the valency of an element is meant the maximum number of atoms with which one atom of the given element can be directly associated in a gaseous molecule, then conclusions about the valency of this or that element must be drawn, at present, only from a study of gaseous molecules. In this case, some of the remarks about the valencies of I, S, &c., in these paragraphs would be rather irrelevant. M. M. P. M.

To obtain the crude earths from *Gadolinite*, Bahr a. Bunsen (*A.* 137, 1) decompose the mineral by HClAq, separate SiO_2 by evaporation to dryness and addition of HClAq, heat to boiling, and ppt. by oxalic acid; they wash the pp., convert the oxalates into nitrates, and ppt. the cerium compounds by addition of K_2SO_4; the earths of the erbium group are then ppd. from the filtrate by oxalic acid, the oxalates are heated in a Pt dish, the carbonates thus obtained are boiled in water (to dissolve out K_2CO_3), and dissolved in HNO_3Aq; oxalic acid is again added, and the ppd. oxalates are once more converted into carbonates by heating; the carbonates are tested for didymium by observing the absorption-spectrum of a very conc. solution in HNO_3Aq; if Di is present the treatment with K_2SO_4 is repeated until a pp. is obtained free from Di; the earths are then ppd. by NH_3Aq free from $(NH_4)_2CO_3$: the pp. is dissolved in HNO_3Aq, and the oxalates are ppd. by addition of oxalic acid. There are different methods for obtaining erbia from the mixed oxalates. Auer v. Welsbach recommends the following (*M.* 4, 630). The oxalates are converted into oxides by heating strongly, the oxides are made into a paste with water and thrown into a quantity of hot nitric acid insufficient for their complete solution; a basic erbium nitrate containing yttria forms on cooling; the process is repeated several times; at last, when there is a considerable quantity of undissolved oxide in the boiling nitric acid, the whole becomes somewhat pasty and greyish-red in colour; the mass is now allowed to cool, and conc. nitric acid is added in small successive quantities until the colour becomes reddish. The acid dissolves compounds of Ce and traces of Fe salts; a compact rose-coloured pp. settles down, from which the mother-liquor can be poured off. The pp. is washed with alcohol with the aid of a filter-pump; the alcohol dissolves nitrates but leaves the basic nitrates. The pp., which consists of basic erbium nitrate containing yttrium nitrate, is purified by a long and tedious process, based on the fact that basic erbium nitrate is produced more readily than the basic yttrium salt by heating the mixed nitrates with the oxides of the metals, and that the basic yttrium salt is more soluble than the erbium salt in liquid containing the normal nitrates. Another method of obtaining basic erbium nitrate consists in heating the mixed nitrates (formed by dissolving the oxides or carbonates in HNO_3Aq) in a Pt dish until red fumes are evolved, and a portion of the residue is insoluble in water; the insoluble portion is again heated, and then treated with water, and so on (Marignac, *A. Ch.* [5] 14, 247; Cleve, *C. R.* 91, 381).

References.—For earlier work *v.* Cleve in Fremy's *Encyclopédie chimique*, tom. 3. Berzelius, *Lehrbuch*, 2 (5th ed.). Mosander, *J. pr.* 30, 27. Bahr a. Bunsen, *A.* 137, 1. Cleve a. Höglund, *Bl.* [2] 18, 193, 289. Lawrence Smith, *C. R.* 87, 146, 831. Marignac, *Ar. Sc.* [3] 3, 413. Delafontaine, *C. R.* 87, 600. Soret, *C. R.* 89, 478, 521; 91, 378. Cleve, *C. R.* 89, 478, 708; 91, 381. Roscoe, *B.* 15, 1274. Marignac, *C. R.* 87, 578. Nilson, *C. R.* 88, 645; 91, 118. De Boisbaudran, *C. R.* 88, 322; 89, 212. Von Welsbach, *M.* 4, 630.

The metal erbium has not yet been isolated. The atomic weight was determined by Delafontaine (*Ar. Sc.* 1866. 112), Cleve a. Höglund (*Bl.* [2] 18, 193, 289), Humpidge a. Burney (*C. J.* 35, 11), but the results were too high. Cleve redetermined the at. w. by synthesising the sulphate from pure Er_2O_3: he obtained the value 166·15 (*C. R.* 89, 706; 91, 381).

So far as the investigation of Er compounds has gone, it shows that this metal is best placed in Group V, in the odd series 9, between Sb and Bi; Er is also analogous to the earth-metals Sc, Y, La, and Yb, and it shows resemblances to Ce (*cf.* NITROGEN GROUP OF ELEMENTS, and EARTHS, METALS OF THE).

Erbium, haloid compounds of. Erbium bromide, chloride, fluoride, and iodide, ErX_3 ($X = Br, Cl, F, I$), have been described; but as the material worked with was not known to be perfectly free from other metals of the yttria group, but little stress can be laid on the descriptions given. These compounds are said to be rose-coloured and deliquescent.

Erbium, oxide of. Er_2O_3. S.G. 8·64. S.H. ·065. S.V.S. 43·98 (Nilson a. Pettersson, *B.* 13, 1459). Emission-spectrum characterised by bright lines 6546 (red), 5631 and 5387 (yellow), 5228 and 5204 (green) (Bahr a. Bunsen, *A.* 137, 1; De Boisbaudran, *C. R.* 76, 1080; 88, 1167, 1342; 89, 212, 516); the dark lines of the absorption-spectrum of the solution of an Er salt correspond with these. Obtained by heating the nitrate or oxalate in air. Pale rose-coloured powder. Not changed when heated in H. Infusible; glows with intense green light when heated, without volatilising. Slowly dissolved by hot HNO_3Aq, H_2SO_4Aq, or HClAq. Does not directly combine with water.

Erbium, salts of. Compounds obtained by replacing H of acids by Er. These salts are formed by dissolving Er_2O_3 in acids; many are also formed by double decomposition from the sulphate or nitrate. Solutions of Er salts are more or less rose-coloured; they generally have an acid reaction with litmus, and taste sweetish but astringent. The salts all belong to the form Er_23X where $X = SO_4$, $2NO_3$, $\frac{2}{3}PO_4$, &c.; a few basic salts, *e.g.* $Er_2O_3.2CO_2$, have been obtained. The principal salts are the *bromate*, *carbonate*, *chlorate* and *perchlorate*, *formate*, *iodate* and *periodate*, *nitrate*, *oxalate*, *selenate* and *selenite*, *sulphate* and *sulphite*, and *phosphate* (*v.* CARBONATES, NITRATES, &c.). M. M. P. M.

ERGOSTERIN $C_{26}H_{40}O$. [154°]. S.G. 1·04. $[\alpha]_D = -114°$. Extracted from ergot of rye (Tanret, *C. R.* 108, 98). Pointed needles (containing aq); sol. alcohol and ether; insol. water. Slowly oxidises in air, very rapidly at 100°. Is not attacked even by hot concentrated alkalis. Resembles cholesterin in many reactions, but gives different results with sulphuric acid and chloroform. The acid dissolves the ergosterin, and agitation with chloroform gives no colouration till evaporation takes place, when a trace of violet appears.

Formyl derivative $C_{28}H_{39}(CHO)O$. [154°]. $[\alpha] = -93·4°$. Spangles, sol. ether.

Acetyl derivative $C_{28}H_{39}AcO$. [169°]. $[\alpha]_D = -80°$. Pearly spangles, sol. ether and alcohol, insol. water.

Butyryl derivative $C_{28}H_{39}(C_4H_9O)O$. [95°]. $[\alpha]_D = -57°$.

ERGOTININE $C_{35}H_{40}N_4O_6$. *Ecboline*. S. (95 p.c. alcohol). ·5 at 20°; 2 at 78°. $[\alpha]_j = 137·5°$. Occurs in ergot of rye, together (according to Dragendorff) with 'scleromucin,' 'sclerotic acid,' 'sclererythrin,' 'sclerocrystallin' $C_{10}H_{10}O_4$, 'scleroxanthin' $C_{10}H_{10}O_4 1\frac{1}{2}aq$, a hydrate of sclerocrystallin, mycose, mannite, cholesterin, leucine, lactic acid, methylamine, and trimethylamine (Wiggers, *A.* 1, 171; Manassewitz, *Z.* [2] 4, 154; Denzel, *Ar. Ph.* [3] 22, 49; Dragendorff, *Ar. Ph.* 7, 32; *C. C.* 1878, 125; Bombelon, *C. C.* 1888, 472). Ergot also contains a fatty oil (Hermann, *Rep. Pharm.* 20, 283; Ganser, *Rep. Pharm.* 20, 301). Tanret (*J. Ph.* 26, 320; *C. J.* 34, 81) also obtained from ergot a crystalline substance, smelling like camphor [165°], (209°), insol. water, sol. alcohol, and chloroform. Kobert (*J.* 1884, 1512) describes ergot as containing cornutine and sphacelic (ergotic) acid.

Preparation.—The ergot is exhausted with alcohol, caustic soda is added to alkaline reaction, the alcohol is distilled off, and the residue agitated with ether. The ethereal extract is then shaken with a concentrated solution of citric acid, the citrate is decomposed by K_2CO_3, and the ergotinine extracted by ether, from which it crystallises. In this way 1·2 g. is got from 1 kilo of ergot (Tanret, *A. Ch.* [5] 17, 499; *C. R.* 81, 896; 86, 888; *cf.* Blumberg, *Ph.* [3] 9, 23, 598).

Properties.—Delicate prismatic needles, turning brown in air. Insol. water, sol. alcohol, ether, and $CHCl_3$. When the ergot is old an amorphous substance (? modification of ergotinine) present, which increases its solubility in alcohol. Its solutions fluoresce violet. The rotatory power of the amorphous ergotinine $[\alpha]_j = 122°$ is less than that of the crystalline variety. Ergotinine gives all the general tests characteristic of alkaloids. When a drop of H_2SO_4 is added to its solution in acetic acid a red colouration passing rapidly to violet and blue is formed. Ergotinine when injected hypodermically produces intoxication.

Salts.—B′HCl.—B′HBr.

ERICIN. A dye-stuff in *Erica vulgaris*. It gives a bronze-green pp. with iron salts, a golden-green pp. with tin salts, and a green colour with copper salts (Savigny a. Collineau, *C. C.* 1881, 703; *C. J.* 42, 309).

ERICINONE $C_{24}H_{24}O_9$ (?). [c. 167°]. An indifferent crystalline substance, said by Uloth (*A.* 111, 215) to be obtained by the dry distillation of ericaceous plants. May be sublimed.

ERICOLIN $C_{26}H_{30}O_3$. A resinous glucoside found in several plants of the heath family, *e.g.* common ling (*Calluna vulgaris*), wild marsh rosemary (*Ledum palustre*), in the red bearberry (*Arctostaphylus uva ursi*), in *Gaultheria procumbens*, in *Epigæa repens*, and in *Rhododendron ferrugineum* (Rochleder a. Schwarz, *A.* 84, 354, 368; Kawalier, *Sitz. W.* 9, 29; Oxley, *Ph.* [3] 2, 1050; Thal, *J.* 1883, 1401). It has a bitter taste. Dilute acids split it up into glucose and ericinol.

Ericinol $C_{20}H_{26}O_2$. Formed, together with glucose, by distilling ericolin or pinipicrin with dilute HCl or H_2SO_4. Volatile oil, turning brown in the air (Rochleder; Kawalier; Thal; Fröhde, *J. pr.* 82, 181). Ericinol takes up water, becoming 'ericinol hydrate' $C_{10}H_{30}O_4$, which has a very characteristic odour (Thal).

ERIGERON OIL. The volatile oil from *Erigeron canadense* contains a terpene ((176). S.G. ^{15} ·848. $[\alpha]_j = 6° 15′$), identical with citrene and hesperidene (Wallach, *A.* 227, 292; *cf.* Vigier a. Cloëz, *J. Ph.* [5] 4, 333).

ERUCIC ACID $C_{22}H_{42}O_2$. *Brassidic acid.* Mol. w. 338. [34°]. An acid occurring as glyceryl ether in colza oil (Welsky, *J. pr.* 58, 449; Staedeler, *A.* 87, 133; Otto, *A.* 127, 182; 135, 226; Haussknecht, *A.* 143, 40), in the fixed oil of white mustard (*Sinapis alba*), and of black mustard (Darby, *A.* 69, 1; Goldschmiedt, *Sitz. W.* [2] 70, 451; 74, 394), and in the fatty oil from grape seeds (Fitz, *B.* 4, 442).

Preparation.—Rape-seed oil is saponified by alcoholic KOH; after distilling off most of the alcohol the fatty acids are precipitated with dilute H_2SO_4, separated, and dissolved in three times the weight of 95 p.c. alcohol; on cooling the solution to 0° the erucic acid crystallises out, and is recrystallised in the same way (Reimer a. Will, *B.* 19, 3320). Long needles (from alcohol). Decomposed by potash-fusion into acetic and arachic acids. Br forms the dibromide $C_{22}H_{42}Br_2O_2$ [46°] (*v.* DI-BROMO-BEHENIC ACID). Nitrous acid converts erucic acid into the isomeric brassic acid (*q. v.*). HI and P at 200° give behenic acid.

Salts.—NaA′.—BaA′$_2$.—PbA′$_2$.—AgA′.

Ethyl ether EtA′: (above 360°); colourless odourless oil; converted by nitrous acid into ethyl brassate.

Glycerin-di-erucic ether $C_3H_5(OH)A'_2$. *Dierucin.* [47°]. Silky colourless crystals (from ether-alcohol). Occurs as a deposit from rapeseed oil after long standing. V. sol. ether and ligroïn, m. sol. hot alcohol, insol. cold alcohol. By nitrous acid it is converted into glycerin-di-brassic ether.

Glycerin-tri-erucic ether $C_3H_5A'_3$. *Trierucin.* [31°]. From erucic acid and glycerin at 300°.

Amide $C_{21}H_{41}.CONH_2$: [84°]; colourless needles; v. sol. ether and benzene, sl. sol. alcohol, insol. water. Formed by the action of NH_3 gas upon the anhydride.

Anilide $C_{21}H_{41}.CO.NHPh$: [55°]; crystals; v. sol. ether and benzene, sl. sol. alcohol.

Anhydride $(C_{21}H_{41}.CO)_2O$: oil which solidifies in a freezing mixture; v. sol. ether and benzene, v. sl. sol. alcohol. Formed by the action of PCl_3 upon erucic acid and subsequent addition of alcohol (Reimer a. Will, *B.* 19, 3320).

ERYTHRENE *v.* BUTINENE.

Erythrene bromide *v.* TETRA-BROMO-BUTANE and DI-BROMO-BUTYLENE.

ERYTHRIN $C_{20}H_{22}O_{10}$ *i.e.* $C_4H_8(C_8H_7O_3)_2O_4$. *Erythric acid.* Mol. w. 422. [137°]. S. ·42 at 100°; S. (ether) ·3 at 20°. Occurs in *Roccella tinctoria*, *R. Montagnei*, *R. fuciformis* and other lichens (Heeren, *Schw. J.* 59, 313; Kane, *A.* 39, 25; Schunck, *A.* 61, 69; Stenhouse, *A.* 68, 72;

Pr. 12, 263; *C. J.* 20, 222; Hesse, *A.* 117, 304; De Luynes, *A. Ch.* [4] 2, 385; Menschutkin, *Bl.* [2] 2, 424). Extracted by milk of lime, and ppd. by HCl. Crystalline mass (containing 1½ aq). Sl. sol. water, v. sol. alcohol and ether. Its alcoholic solution gives a violet colour with Fe_2Cl_6.

Reactions.—1. Boiling *water* or *alkalis* split it up into orsellic acid $C_8H_8O_4$ and picroerythrin $C_{12}H_{16}O_7$; the orsellic acid being resolved by longer boiling into CO_2 and orcin. Boiling *alcohol* produces, in the same way, orsellic ether and picroerythrin. Methyl and amyl alcohols act in like manner.—2. Boiling with excess of lime-water gives erythrite, orcin, and CO_2 (Lamparter, *A.* 134, 255).—3. *Bromine* forms $C_{20}H_{18}Br_4O_{10}$.

Metallic derivatives.—$C_{20}H_{20}PbO_{10}$ *x*aq. $Pb_3(C_{20}H_{19}O_{10})_2$ 3aq.—$C_{20}H_{18}Pb_2O_{10}$.—$Pb_5(C_{20}H_{17}O_{10})_2$.

(β)-Erythrin $C_{21}H_{24}O_{10}$. Occurs in *Roccella fuciformis* (Menschutkin, *Bl.* [2] 2, 424). White crystalline powder (containing aq). Nearly insol. water, sol. alcohol, and ether. Decomposed by boiling alcohol or water into orsellic ether or acid and (β)-picroerythrin. Boiling baryta splits it up into erythrite, CO_2, and betorcin.—$Pb_2C_{21}H_{20}O_{10}$.

Erythrin *v.* BROMO-FLUORESCEÏN.

ERYTHRITE $C_4H_{10}O_4$ *i.e.* $CH_2(OH).CH(OH).CH(OH).CH_2(OH)$. *Erythrol. Erythromannite. Erythroglucin. Eryglucin. Phyoite.* Mol. w. 122. [112°]. (330°). S.G. 1·45 (Schröder, *B.* 12, 562). R_∞ 43·65 (in a 14 p.c. aqueous solution) (Kanonnikoff, *J. R.* 15, 449). *Heat of solution* −5200 at 9° (Colson, *C. R.* 104, 113). Occurs ready-formed in *Protococcus vulgaris* and is produced by the action of boiling lime or baryta upon erythrin or picroerythrin (Stenhouse, *Tr.* 1848, 76; 1849, 399; Strecker, *A.* 68, 111; Schunck, *P. M.* 7, 33, 254; Lamy, *A. Ch.* [3] 35, 138; 51, 232; Wagner, *J. pr.* 61, 125; Hesse, *A.* 117, 327; Hofmann, *B.* 7, 512; De Luynes, *A. Ch.* [4] 2, 339; *C. R.* 56, 803).

Properties.—Large dimetric crystals with sweet taste. Inactive. Neutral to litmus. V. sol. water, sl. sol. cold alcohol, insol. ether. Does not reduce Fehling's solution. Is not ppd. by lead subacetate. Its aqueous solution dissolves lime, a pp. being formed on boiling or on adding alcohol. Does not undergo alcoholic fermentation. Like other polyhydric alcohols, it renders a solution of borax acid (Dunstan, *Ph.* [3] 13, 257). In presence of vegetable mould it undergoes butyric fermentation (Fitz, *B.* 11, 1890; 12, 475). Erythrite does not react when heated with aldehyde or isobutyric aldehyde at 125° (Lochert, *A. Ch.* [6] 16, 64).

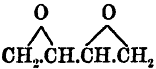
Reactions.—1. *Potash-fusion* gives acetic and oxalic acids.—2. Fuming *nitric acid* forms the nitrate. Dilute nitric acid oxidises it to oxalic and tartaric acids (Przybytek, *Bl.* [2] 35, 108); at the same time there is formed an aldehyde or ketone whose phenyl-hydrazide $C_{16}H_{18}N_4O_2$ melts at [167°] (Fischer a. Tafel, *B.* 20, 1088).—3. CrO_3 and $KMnO_4$ give formic and oxalic acids. $4H_2SO_4$ forms a sulphuric acid $C_8H_{11}O_2(SO_4H)_3$ (Hesse, *A.* 117, 329). The salts $Ca_3A'''_2$6aq, $Ba_3A'''_2$6aq, and $Pb_3A'''_2$12aq have been described.—4. Heating with aqueous HI forms secondary butyl iodide.—5. PBr_5 gives $C_4H_6Br_4$ [112°] (Colson, *C. R.* 104, 113).—6. Yields thiophene by heating with P_2S_5 (Paal a. Tafel, *B.* 18, 688).—7. Distillation with S_2Cl_2 under 100mm. pressure yields a substance (? $C_4H_8SO_4$) which crystallises from ether in needles [115°] (Henninger, *A. Ch.* [6] 7, 231).—8. *Formic acid* produces several formins, including the crystalline tetraformin $C_4H_6(O.CHO)_4$. When the mixture of formins is distilled at 250° there is given off CO_2, butinene, and CO, and a liquid distils over consisting of water, formic acid, crotonic aldehyde, di-oxy-butylene (crotonylene glycol), $C_4H_6(OH)_2$ 'dihydrofurfurane' (C_4H_8O), (67°), and the anhydride of erythrite $C_4H_8O_3$ (Henninger, *C. R.* 98, 149; *A. Ch.* [6] 7, 210; *Bl.* [2] 19, 2, 145; 21, 242).—9. *Phenyl cyanate* (4 mols.) heated with erythrite (1 mol.) forms $C_4H_6(O.CO.NHPh)_4$ [215°] a microcrystalline solid, sl. sol. alcohol and ether (Tessmer, *B.* 18, 970).

First Anhydride $C_4H_8O_3$. *Erythrane.* (155°) at 18 mm.

Formation.—1. A product of the action of formic acid on erythrite.—2. By heating erythrite with equal weights of water and conc. H_2SO_4.—3. In small quantity by the action of HCl on erythrite.

Properties.—Liquid. Conc. HCl converts it into erythrite dichlorohydrin (Henninger, *A. Ch.* [6] 7, 225).

Second Anhydride $C_4H_6O_2$ *i.e.*



$$\overset{\frown O \frown}{CH_2.CH}.\overset{\frown O \frown}{CH.CH_2}$$

(?). *Erythrite dioxide. Erythrane.* (138°). S.G. $^{\underline{0}}$ 1·132; $^{\underline{18}}$ 1·113. C.E. (0°–18°) ·00095. V.D. 3·16 (obs.). Formed by treating erythrite dichlorhydrin in ethereal solution with KOH, the yield being 70 p.c. (Pryzbytek, *B.* 17, 1092; *Bl.* [2] 41, 393; 42, 322). Mobile liquid, miscible with water. Slowly unites with water to form erythrite. Combines with HCl reproducing the dichlorhydrin. Unites with HCN to form the nitrile of di-oxy-adipic acid. Readily combines with NH_3 and amines. Aniline forms a compound $C_{16}H_{20}N_2O_2$. Reduces $AgNO_3$ forming a mirror. Ppts. MgO from magnesium salts.

Isomeride of the Second Anhydride $C_4H_6O_2$. [173°]. Formed, together with $C_4H_6(OH)(OEt)_2$, by the action of NaOEt upon erythrite dichlorhydrin, or by treating the dichlorhydrin with powdered NaOH (Henninger, *A. Ch.* [6] 7, 225). Plates (from alcohol).

Di-ethyl ether $C_4H_6(OH)_2(OEt)_2$. [13·5°]. (144°) at 22 mm. From the dichlorhydrin and NaOEt at 100° (Henninger, *A. Ch.* [6] 7, 230).

Erythrite tetranitrate $C_4H_6(NO_3)_4$. *Nitro-erythrite.* [61°]. Formed by dissolving erythrite in cold fuming HNO_3 and ppg. by the addition of H_2SO_4 (Stenhouse, *Tr.* 1849, 399). Large plates (from alcohol). Insol. cold water. Explodes when struck. Alcoholic ammonium sulphide reconverts it into erythrite.

Erythrite tetra-sulphuric acid $C_4H_6(SO_4H)_4$. Deliquescent crystals got by dissolving erythrite in $ClSO_3H$. Boiling water slowly resolves it into erythrite and hydric sulphate (Claesson, *J. pr.* [2] 20, 7).

Salts.—K_4A'''',4aq. Nearly insol. cold water. BaA''',4aq. Insol. water. Ppd. by adding $BaCl_2$ to a solution of the free acid but not to one of the potassium salt (Claesson).

Mono-formyl derivative $C_4H_6(OH)_3(O.CHO)$. *Erythrite monoformin.* (192°). Formed, together with the following, by boiling erythrite (1 pt.) with formic acid (2½ pts.) for 6 hours (Henninger, *A. Ch.* [6] 7, 215).

Tetra-formyl derivative $C_4H_6(O.CHO)_4$. [150°]. Prepared by heating erythrite with formic acid at 200° and extracting with dry ether; the product being treated in the same way with 20 pts. of formic acid (S.G. 1·18). Long needles (from alcohol).

Benzoyl derivative $C_4H_6(OH)_3(OBz)$. From erythrite and HOBz at 250° (Berthelot, *Chimie organique*. 2, 224). Crystalline mass, insol. water, v. sol. alcohol and ether.

Tetra-benzoyl derivative $C_4H_6(OBz)_4$. From the preceding (1 pt.) and HOBz (15 pts.) at 200° (B.). Nearly insol. water.

Orsellyl derivative $C_{12}H_{16}O_7$ *i.e.* $C_4H_6(OH)_3(O.CO.C_6H_2(OH)_2Me)$. *Picroerythrin.* [158°]. Obtained by boiling erythrin with water, alcohols, or alkalis (Schunck, *A.* 61, 64; Stenhouse, *A.* 68, 76; Hesse, *A.* 117, 321). Silky prisms (containing 3aq). Tastes bitter. V. e. sol. hot water. Decomposed by boiling lime-water into erythrite, orcin, and CO_2. Gives a purple colour with Fe_2Cl_6.

(β)-*Orsellyl derivative. Anhydride.* $C_{13}H_{16}O_6$. (β)-*Picroerythrin.* Obtained by boiling (β)-erythrin with alcohol (Menschutkin, *Bl.* [2] 2, 424). Needles, v. e. sol. water and alcohol, insol. ether. Reduces hot silver solution. Split up by boiling with baryta into CO_2 erythrite, and betorcin $C_8H_{10}O_2$.

Erythrite chlorhydrin $C_4H_8(OH)_3Cl$. [66°]. Flat interlacing needles, sol. alcohol, insol. ether.

Erythrite dichlorhydrin $C_4H_8(OH)_2Cl_2$. [126°]. (152°) at 30 mm. Prepared by heating erythrite (200 g.) with conc. HClAq (2400 g.) for 6 hours, and distilling the product under reduced pressure. Arborescent mass of crystals, v. sol. alcohol (Henninger, *A. Ch.* [6] 7, 228; Przybytek, *B.* 17, 1091). A mixture of HNO_3 and H_2SO_4 converts it into the nitrate $C_4H_6(NO_3)_2Cl_2$ [60°] (Champion, *C. R.* 73, 114).

Erythrite tetrachlorhydrin *v.* TETRA-CHLORO-BUTANE.

Erythrite dibromhydrin $C_4H_6(OH)_2Br_2$. [130°]. From erythrite and conc. HBrAq at 110° (Champion, *Z.* 1871, 348; *C. R.* 73, 114). Crystals (from ether), insol. water. A cold mixture of fuming HNO_3 (1 pt.) and conc. H_2SO_4 (2 pts.) forms the nitrate $C_4H_6(NO_3)_2Br_2$ [75°].

ERYTHROCENTAURIN $C_{27}H_{24}O_8$. [136°]. S. ·06 at 15°; 7 at 100°; S. (86 p.c. alcohol) 2; S. (ether) ·4; S. (chloroform) 7. A substance allied to santonin which may be extracted by alcohol from the common centaury (*Erythræa Centaurium*). Tasteless crystals (from ether); neutral to litmus. Inactive. Sol. most menstrua; water ppts. it unaltered from its solution in H_2SO_4. It turns bright red in sunlight, being affected by the blue or violet rays; the red colour disappears on solution or on heating to 130° (Mehu, *J. Ph.* [4] 3, 265).

ERYTHROGLUCIC ACID $C_4H_8O_5$ *i.e.* $CH_2(OH).CH(OH).CH(OH).CO_2H$. Obtained by the oxidation of erythrite by air in presence of platinum-black or by nitric acid (Sell, *Bl.* [2] 5, 384; Lamparter, *A.* 134, 243). Deliquescent mass; v. sol. water and alcohol.—$BaC_4H_6O_5$ aq (L.).—$(C_4H_6PbO_5)_4PbO_2H_2$(S.).—$C_4H_6PbO_5$ (at 160°; L.).

ERYTHRO-OXY-ANTHRAQUINONE *v.* OXY-ANTHRAQUINONE.

ERYTHROPHLEÏNE. An alkaloid in the bark of *Erythrophlœum guineense* (Gallois a. Hardy, *Bl.* [2] 26, 39). Sol. alcohol, sl. sol. ether. Gives a violet colour with MnO_2 and H_2SO_4.

ESENBECKINE. An alkaloid in the bark of *Esenbeckia febrifuga* (Buchner, *Rep. Pharm.* 31, 481; 37, 1; Am Ende, *Ar. Ph.* [2] 143, 112).

ESERINE $C_{15}H_{21}N_3O_2$. *Phytostigmine.* [45°]. An alkaloid which may be extracted by moist alcohol from Calabar beans (Petit, *J. Ph.* [4] 14, 255; *C. R.* 72, 569; Hesse, *A.* 129, 115; 141, 82). Resinous; v. sol. alcohol, ether, benzene, and $CHCl_3$; m. sol. water. Alkaline to litmus. Poisonous, producing contraction of the pupil. The sulphate evaporated with ammonia leaves a blue residue. Bleaching powder colours its solution red.—$B'HIHgI_2$. [70°] (H.).

ESSENTIAL OILS. Oils, usually obtained from plants, which are volatile either alone or with steam. They usually contain one or more hydrocarbons such as terpenes (*q. v.*) and one or more substances containing oxygen, which sometimes separate in a solid form on cooling strongly and are then called stearoptenes, the remaining liquid being termed elæoptene (*v.* also OILS).

ESTER. A name applied by Gmelin to compound ethers derived from oxygenated acids to distinguish them from simple and mixed ethers.

ETHALDEHYDE *v.* ALDEHYDE.

ETHANE C_2H_6 *i.e.* $CH_3.CH_3$. *Di-methyl-ethyl hydride.* Mol. w. 30. S. ·0871 at 0° (Bunsen); S. (alcohol) 1·5 (Berthelot, *J.* 1867, 344). H.F.p. 25,670 (Thomsen, *J. pr.* [2] 23, 158); 28,560 (*Th.*); 28,000 (Dulong; Favre a. Silbermann). H.F.v. 24,510 (Thomsen); 27,400 (*Th.*).

Occurrence.—In the gases given off by natural petroleum (Smith, *A. Ch.* [5] 8, 566).

Formation.—1. By the action of methyl iodide upon zinc or sodium (Frankland, *C. J.* 2, 173; *A.* 71, 213; Wanklyn a. Buckeisen, *A.* 116, 329).—2. By heating propionitrile with potassium (Frankland a. Kolbe, *C. J.* 1, 60; *A.* 65, 269).—3. By the electrolysis of potassium acetate (Kolbe, *A.* 69, 279).—4. By the action of water on zinc ethyl (Frankland, *C. J.* 3, 338; *A.* 71, 203; 85, 360; 95, 53).—5. By heating ethyl iodide (9 pts.) with Al_2Cl_6 (2·6 pts.) at 150° (Köhnlein, *B.* 16, 562).—6. In small quantity together with methane and CO_2 by heating Ac_2O with BaO_2 (Schützenberger, *Bl.* [2] 5, 278; Darling, *C. J.* 21, 496).—7. From $HgEt_2$ and H_2SO_4 (Schorlemmer, *A.* 132, 234).—8. From EtI, alcohol, and zinc-dust (Sabanejeff, *B.* 9, 1810).

Preparation.—By dropping a mixture of equal volumes of ethyl iodide and absolute alcohol upon the copper-zinc couple, the gas being passed through a scrubber containing copper-zinc, through alcoholic NaOH, through bromine-water, through caustic soda, and finally through slaked lime (Percy Frankland, *C. J.* 47, 236).

Properties.—Colourless gas. Burns with pale flame. With water under pressure it forms a crystalline hydrate (Villard, *C. R.* 106, 1602). The identity of ethane from $ZnEt_2$ with that from KOAc may be shown by chlorination, both yielding ethyl chloride (Schorlemmer, *A.* 131, 76; 132, 234) or by their heats of combustion (Thomsen, *J. pr.* [2] 23, 158).

Derivatives *v.* BROMO-, BROMO-IODO-, BROMO-NITRO-, CHLORO-, CHLORO-IODO-, CHLORO-NITRO-, NITRO-ETHANES, &c.

ETHANE-ARSONIC ACID *v.* ARSENIC COMPOUNDS, ORGANIC.

ETHANE-TRICARBOXYLIC ACID $CO_2H.CH_2.CH(CO_2H)_2$. [159°]. From the ether by conc. KOHAq. Formed also by saponifying ethane tetra-carboxylic acid and from bromo-succinic ether by successive treatment with alcoholic KCy and KOH (Orlowsky, *J. R.* 9, 278; *B.* 9, 1604). Small hard prisms (from ether). V. sol. alcohol, ether, or water, sl. sol. benzene. When melted it splits up into CO_2 and succinic acid.

Salts.—The ammonium salt gives pps. with $BaCl_2$ or $Pb(OAc)_2$ in the cold, and with $CaCl_2$ or $FeCl_2$ on warming.—$Ca_3A'''_2$.—$Zn_3A'''_2 2aq$.—Ag_3A'''.

Ethyl ether $CO_2Et.CH_2.CH(CO_2Et)_2$. (278° uncor.). S.G. $\frac{17}{15}$ 1·089. From malonic ether, NaOEt, alcohol, and chloro-acetic ether (Bischoff, *A.* 214, 38). Oil. V. e. sol. alcohol or ether. By the action of Cl on the ether chloro-ethane-tricarboxylic ether is formed, which on boiling with HCl gives fumaric acid, and with KOH gives malic acid. By the successive action of sodium and chloro-acetic-ether on the ether, the ether of propane-tetra-carboxylic acid $(CO_2H)CH_2.C(CO_2H)_2.CH_2(CO_2H)$ is formed, and this acid on heating gives CO_2 and tricarballylic acid $(CO_2H)CH_2.CH(CO_2H).CH_2(CO_2H)$ (Bischoff, *B.* 13, 2161).

First nitrile *v.* CYANO-SUCCINIC ETHER.

Ethane tetra-carboxylic acid $C_6H_6O_8$ *i.e.* $(CO_2H)_2CH.CH(CO_2H)_2$.

Acetylene tetra-carboxylic acid.

Di-ethyl ether $CO_2Et.CH(CO_2H).CH(CO_2H).CO_2Et$. [133°]. The potassium salt is formed as a sticky pp. by the action of KOH (36 g.) on the tetra-ethyl ether (28 g.) dissolved in alcohol (720 g.) at 0°. Plates with obtuse angles. Deliquescent, v. sol. alcohol or ether, sl. sol. chloroform or CS_2. When heated, it splits off CO_2, becoming succinic ether (Guthzeit, *A.* 214, 72). The salt Na_2Et_2A'''' is converted by di-bromo-*o*-xylene $C_6H_4(CH_2Br)_2$ into naphthalene tetra-hydride tetracarboxylic acid (Baeyer a. Perkin, *B.* 17, 449).

Tetra-ethyl ether Et_4A''''. [76°]. (305°). From malonic ether, chloro-malonic ether, NaOEt and alcohol (Conrad a. Bischoff, *A.* 214, 68; *B.* 13, 601; 21, 2087). Formed also by the action of iodine (1 mol.) on sodio-malonic ether (2 mols.), dissolved in absolute alcohol (Bischoff a. Rach, *B.* 17, 2781). Needles. V. sol. alcohol, ether or benzene.

Reactions.—1. Very stable. NaOEt and benzyl chloride do not form a benzyl derivative. 2. Heated with aqueous HCl, or with aqueous KOH, it forms CO_2, ethane tri-carboxylic acid and alcohol.

Amide $C_2H_2(CONH_2)_4$. Crystals, v. sl. sol. water. Decomposes above 230°.

ETHANE-PHOSPHONIC ACID $C_2H_5.PO(OH)_2$. [44°]. From ethyl-phosphine and fuming HNO_3 (Hofmann, *B.* 5, 106). Crystals, v. e. sol. water.—Ag_2A'': amorphous yellow powder.

Chloride $C_2H_5.POCl_2$. (c. 175°). Liquid (Michaelis, *B.* 13, 2174).

ETHANE-SELINIC ACID *v.* SELENIUM COMPOUNDS, ORGANIC.

ETHANE-SULPHINIC ACID $C_2H_5.SO_2H$. *Ethyl-sulphinic acid.*

Formation.—1. By the action of $ZnEt_2$ followed by water upon SO_2 (Wischin, *A.* 139, 364).—2. From ethane-sulphonic chloride and zinc-dust (Pauly, *B.* 10, 941).—3. By the oxidation of sodium mercaptide NaSEt.—4. From $PbEt_4$ and SO_2 (Frankland a. Lawrance, *C. J.* 35, 246).

Properties.—Syrup. Gives ethane-sulphonic acid when oxidised by HNO_3 (Claesson, *J. pr.* [2] 15, 222) and a compound $C_6H_{15}NS_3O_7$ [81°] (Zuckschwerdt, *A.* 174, 308).

Salts.—NaA′: crystals (from alcohol).—$BaA'_2 aq$.—$ZnA'_2 aq$.—PbA'_2. From $PbEt_4$ and SO_2 (Frankland a. Laurance, *B.* 12, 846).—AgA′: laminæ, m. sol. water.

Ethane di-sulphinic acid $C_2H_6S_2O_4$ *i.e.* $C_2H_4(SO_2H)_2$.

Ethylene-disulphinic acid. From ethane disulphonic chloride $C_2H_4(SO_2Cl)_2$, zinc-dust and water (Otto, *J. pr.* [2] 36, 439). The free acid is unstable.

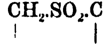
Salts.—$Na_2A'' 4aq$: small laminæ from alcohol), v. e. sol. water, sl. sol. alcohol.—ZnA'_2: small plates, sl. sol. cold, v. sol. hot water.

Di-methyl ether Me_2A''. [190°]. *Di-methyl ethylene disulphone.* From the sodium salt and MeBr. Plates, insol. cold, sol. hot water and alcohol.

Di-ethyl ether Et_2A''. [137°]. *Ethylene diethyl sulphone.* From Na_2A'' and EtBr (Otto, *J. pr.* [2] 36, 436). Needles. Sl. sol. ether, benzene, chloroform and CS_2, v. sol. hot alcohol. Converted by PCl_5 into $C_2H_4(SO_2Cl)_2$ [91°]. Reduced in alkaline solution to ethane sulphinic acid. Aqueous KOH forms $C_2H_4(OH)(SO_2Et)$ and ethane-sulphonic acid. Ammonia forms a substance [83°].

Di-propyl ether Pr_2A''. [155°]. From Na_2A'' and BrPr (Otto). Iridescent plates.

Ethylene ether C_2H_4A'' *i.e.*



$$\begin{array}{l} CH_2.SO_2.CH_2 \\ | \qquad\qquad | \\ CH_2.SO_2.CH_2 \end{array}.$$

From Na_2A'' and ethylene bromide (Otto, *J. pr.* [2] 36, 446). Prisms, insol. ordinary solvents, m. sol. hot conc. HNO_3.

ETHANE SULPHONIC ACID $C_2H_5SO_3H$. *Ethyl sulphonic acid.*

Formation.—1. By the oxidation of mercaptan, of ethyl sulphocyanide, or of di-ethyl disulphide (Löwig a. Weidmann, *P.* 47, 153; 49, 329; Kopp, *A.* 35, 346; Muspratt, *C. J.* 3, 18). 2. From K_2SO_3 and EtI (Strecker, *A.* 148, 90; Graebe, *A.* 146, 37).

Properties.—Deliquescent mass. Not acted on by Cl, but converted by ICl_3 into $C_2H_3Cl_2SO_3H$ and C_2Cl_6 (Spring a. Winssinger, *B.* 15, 445).

Salts.—NaA′ *x*aq.—NaA′$\frac{1}{4}$NaI (Bender, *A.* 148, 90).—KA′aq.—$CaA'_2 x aq$.—$BaA'_2 aq$.—$ZnA'_2 7aq$.—$CuA'_2 5aq$.—$HgA'_2 HgO$ (Claesson, *A.* 148, 90).—$PbA'_2 aq$.—AgA′.

Methyl ether MeA′. (c. 199°). From ethane-sulphonic chloride and NaOMe (Carius, *J. pr.* [2] 2, 262).

Ethyl ether EtA′. Mol. w. 138. (213° cor.). S.G. $\frac{0}{0}$ 1·1712; $\frac{20}{4}$ 1·1452. R_∞ 29·79. From

$C_2H_5.SO_2Cl$ and NaOEt (C.); or from EtI and Ag_2SO_3 (Kurbatoff, *A.* 173, 7; Nasini, *B.* 15, 2884; *G.* 13, 304).

Chloride $C_2H_5SO_2Cl$. (178° cor.). S.G. $^{\underline{22.5}}$ 1·357. From the sodium salt and PCl_5 (Gerhardt a. Chancel, *C. R.* 35, 691). Also from di-ethyl sulphoxide and chlorine in presence of water (S. a. W.). PCl_5 decomposes it into EtCl and $SOCl_2$.

Amide $C_2H_5SO_2NH_2$. [58°]. Silky needles or long prisms (from ether). Sol. water, alcohol and ether (James, *C. J.* 43, 43)

Methylamide $C_2H_5.SO_2NHMe$. (276°). S.G. $^{\underline{15}}$ 1·216. From the chloride and methylamine, both being dissolved in cold ether (Franchimont a. Klobbie, *R. T. C.* 5, 274). Liquid, miscible with water. When poured into 5 pts. of fuming HNO_3 (S.G. 1·5) it forms a nitramide $C_2H_5.SO_2.N(NO_2)Me$ [11°], a liquid which deflagrates at 100° and is sl. sol. cold water. The nitramide is volatile with steam.

Di-methyl-amide $C_2H_5SO_2NMe_2$. (240°). S.G. $^{\underline{15}}$ 1·146. Liquid, miscible with water. When poured into 5 vols. of HNO_3 (S.G. 1·5) it gives di-methyl-nitramine NMe_2NO_2.

Ethyl-amide $C_2H_5.SO_2.NHEt$. (272°). S.G. $^{\underline{15}}$ 1·154. Liquid, miscible with water, sol. ether. HNO_3 (S.G. 1·5) gives the nitramide $C_2H_5.SO_2.NEt.NO_2$ [20°], a crystalline substance sl. sol. cold water, volatile with steam.

Di-ethyl-amide $C_2H_5.SO_2.NEt_2$. (254°). S.G. $^{\underline{15}}$ 1·080. Liquid, with characteristic odour, sol. ether, sol. water, but not miscible therewith. Fuming HNO_3 (S.G. 1·5) gives $C_2H_5.SO_2.NEt.NO_2$ (F. a. K.).

***s*-Ethane-disulphonic acid** $SO_3H.CH_2.CH_2.SO_3H$. *Ethylene disulphonic acid.* [94°] (when anhydrous).

Formation.—1. Together with sulpho-propionic acid and CO_2, by heating propionamide or propionitrile with fuming H_2SO_4 (Buckton a. Hofmann, *C. J.* 9, 250; *A.* 100, 129).—2. By the action of fuming nitric acid upon ethylene thiocarbonate $C_2H_4CS_3$ (Husemann, *A.* 126, 269) or upon $C_2H_4(SH)_2$.—3. From nitro-ethane and fuming H_2SO_4 (Meyer a. Wurster, *B.* 11, 1168).

Properties.—Deliquescent mass of radiating crystals (containing aq). Potash-fusion gives acetylene (Berthelot, *Z.* 1869, 682).

Salts.—$(NH_4)_2A'$: long monoclinic prisms. —K_2A'': thick, four-sided, monoclinic prisms. S. 38 at 17°.—KHA'' $1\frac{1}{2}$aq: hard crystalline crusts. —Na_2A'' 2aq. S. ·023 at 21° (Guareschi, *G.* 9, 88).—Ag_2A'': thin monoclinic tables. — $Ag_3HA''_2$ 12aq.—BaA''aq: stellate groups of six-sided tablets (B. a. H.).—BaA'': monoclinic prisms; ppd. by alcohol, or from water. S. 2·85 at 17° (G.).—BaA'' 2aq: trimetric octahedra (Husemann).—CaA''.—CuA'' 4aq: monoclinic light-blue prisms.—PbA'' $1\frac{1}{2}$aq: easily soluble crystals.—PbA'' 2aq.—MgA'' 6aq.—HgA'' 6aq: long thin monoclinic prisms.—Hg_2A''aq: white crusts, which separate on warming into an acid and a basic salt.—ZnA'' 6aq: nacreous monoclinic tables.

Chloride $C_2H_4(SO_2Cl)_2$. [91°]. Needles (from ether). Boiling alcohol decomposes it, giving off SO_2 and EtCl (Königs, *B.* 7, 1163).

***u*-Ethane disulphonic acid** $CH_3.CH(SO_3H)_2$. *Ethylidene disulphonic acid.* Obtained by oxidising thio-aldehyde $(C_2H_4S)_3$ or thialdine by $KMnO_4$ (Guareschi, *G.* 9, 75; *A.* 222, 302). Syrup, v. sol. water and alcohol.

Salts.—Na_2A''aq: tables, nearly insol. alcohol.—K_2A'' 2aq: prisms (from water).—K_2A'': needles, ppd. by adding alcohol to its aqueous solution. S. 64 at 17°.—MgA'' 5aq.—CaA''.—BaA'' 3aq: tables (from water). S. (of BaA'') 11 at 17°.—BaA'' $3\frac{1}{2}$aq: ppd. by alcohol.—CaA'' 2aq.—CuA'' aq.—Ag_2A'' aq: slender needles.

Ethyl ether Et_2A''. From Ag_2A'' and EtI (Mauzelius, *B.* 21, 1551). Reddish oil, insol. alkalis, v. sol. alcohol and ether. With NaOEt it gives $CH_3.CNa(SO_3Et)_2$, whence EtI gives butane disulphonic ether.

Ethane-tri-sulphonic acid $CH_2(SO_3H).CH(SO_3H)_2$. '*Ethenyl-tri-sulphonic acid.*' Formed by boiling tri-chloro-ethane (chloro-ethylene dichloride) with a saturated aqueous solution of neutral ammonium sulphite (Monari, *B.* 18, 1346). Large hexagonal tables. V. sol. water and alcohol. Strongly acid.

Salts.—$A'''Na_3$ 4aq: large six-sided tables.—$A'''(NH_4)_3$: large prisms.—A'''_2Ba_3 $5\frac{1}{2}$aq: octahedral crystals, somewhat sol. water.

ETHANE-THIO-SULPHONIC ACID $C_2H_5.SO_2.SH$. Prepared by the action of K_2S on ethane-sulphonic chloride (Spring, *B.* 7, 1162).

Ethyl ether $C_2H_5.SO_2.SC_2H_5$. *Ethyl-disulphoxide.* (130°–140°). S.G. 1·24. Prepared by the action of C_2H_5Br on the potassium salt (Otto, *B.* 15, 122; 11, 2073). Formed also by heating mercaptan or Et_2S_2 with nitric acid (S.G. 1·23) (Löwig a. Weidmann, *A.* 35, 343; Lukaschewitch, *Z.* 1868, 641). Oil, smelling of onions; volatile with steam; v. sol. alcohol and ether, insol. ligroin. Further oxidation by HNO_3 converts it into ethane-sulphonic acid. Zinc and dilute H_2SO_4 reduce it to mercaptan. Aqueous potash forms Et_2S_2, ethane sulphonic acid, and ethane sulphinic acid (Pauly a. Otto, *B.* 11, 2073).

ETHENYL. The trivalent radicle $CH_3.C\vdots$ Vinyl is the name given to the isomeric monovalent radicle $CH_2{:}CH$.

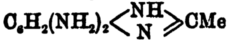
ETHENYL-AMIDINE *v.* ACETAMIDINE.

ETHENYL-AMIDO-BENZAMIDE *v.* OXY-METHYL-QUINAZOLINE.

ETHENYL TRI-AMIDO-BENZENE $C_6H_3(NH_2)(N_2HC_2H_3)$. The hydrochloride of this base $B'H_2Cl_2$ $1\frac{1}{2}$aq, formed by the action of HCl on its acetyl derivative, crystallises in easily soluble lustrous crystals.

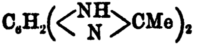
Acetyl derivative $C_6H_3(NHAc)(N_2HC_2H_3)$ 2aq. [85°–90°] (above 360°). From tri-amido-benzene and Ac_2O (Salkowski a. Rudolph, *B.* 10, 1692). Geodes of prisms (from water); v. sl. sol. cold water.

Ethenyl-tetra-amido-benzene $C_8H_{10}N_4$ *i.e.*



$C_6H_2(NH_2)_2<\begin{matrix}NH\\N\end{matrix}\gg CMe$ [1:2:3:4]. Formed by reduction of nitro-ethenyl-tri-amido-benzene. The free base is at once oxidised by the air to brown bodies. With quinones it forms quinoxalines.—$B''H_2Cl_2$: colourless plates. The picrate forms sparingly soluble yellow needles (Nietzki a. Hagenbach, *B.* 20, 333).

Di-ethenyl-tetra-amido-benzene $C_{10}H_{10}N_4$ *i.e.*



$C_6H_2\left(<\begin{matrix}NH\\N\end{matrix}>CMe\right)_2$ [1:2:3:4]. [210°]. Long colourless needles (containing aq). V. sol. alcohol and hot water, sl. sol. cold water, nearly insol. ether. Formed by reduction of di-nitro-di-acetyl-*p*-phenylene-diamine with tin and HCl. It is a very stable body and cannot be saponified.

Salts.—$B''H_2Cl_2$aq: colourless soluble crystals.—$B''H_2Cl_2PtCl_4$ 2aq: long yellow needles.—$B''H_2SO_4$aq: colourless needles. — Picrate $B''C_6H_2(NO_2)_3OH$: yellow needles (Nietzki a. Hagenbach, *B.* 20, 329).

Di-ethenyl-tetra-amido-benzene $C_{10}H_{10}N_4$ *i.e.* $C_6H_2\left(<\substack{NH\\N}>CMe\right)_2$ [1:2:4:5]. (above 360°). Colourless needles. Formed by reduction of di-acetyl-di-nitro-*m*-phenylene-diamine.

Salts.—$B''H_2SO_4$: colourless needles.—$B''H_2Cl_2PtCl_4$Aq: yellow needles (Nietzki a. Hagenbach, *B.* 20, 336).

ETHENYL-DI-AMIDO-BENZOIC ACID $C_6H_3(CO_2H)<\substack{N\\NH}>C.CH_3$ [1:3:4]. *Ethenyl-o-phenylene-diamine carboxylic acid.* [c. 302°]. Formed by reduction of *m*-nitro-*p*-acetamido-benzoic acid [221°], or of *p*-nitro-*m*-acetamido-benzoic acid [206°], with tin and acetic acid (Kaiser, *B.* 18, 2944). White needles (containing aq). V. sol. hot acetic acid, less sol. hot alcohol, nearly insol. ether, acetone, benzene, and chloroform.

Salts.—A'K: very soluble microscopic needles.—A'H,HCl ½aq: easily soluble fine white needles. — $(A'H,HCl)_2PtCl_4$ 2aq: thick yellow needles, sol. hot, sl. sol. cold, water.

ETHENYL-AMIDO-*p*-CRESOL $\left[1\,\substack{4\\3}\right]$ $C_6H_3(CH_3)<\substack{O\\N}>C.CH_3$. (219° uncor.). Formed by boiling the hydrochloride of amido-*p*-cresol with acetic anhydride and sodium acetate (Nölting a. Kohn, *B.* 17, 361). Liquid. Sol. alcohol, ether, and aqueous acids, v. sl. sol. water.

Salts.—B'HCl×: very soluble white crystalline powder.—$B'_2H_2Cl_2PtCl_4$: yellow powder, sol. water and alcohol.

ETHENYL-TRI-AMIDO-ψ-CUMENE *v.* AMIDO-ψ-CUMYLENE-ACETAMIDINE.

ETHENYL-TRI-AMIDO-NAPHTHALENE $C_{12}H_{11}N_3$ *i.e.* $NH_2.C_{10}H_5<\substack{N\\NH}>C.CH_3$. From the acetyl derivative of di-nitro-(α)-naphthylamine by reduction with tin and HCl (Meldola a. Streatfeild, *C. J.* 51, 692). The free base is extremely soluble in water, and is rapidly oxidised by exposure of its solution to the air. Aqueous solutions of its salts are oxidised by air.

Salts.—$B''H_2SO_4$ ½aq.—$B''H_2Cl_2$ 1½aq: stellate aggregates of thick stumpy needles.—$B''H_2Cl_2$ ½aq: long white needles.—$B''H_2PtCl_6$.—$B''H_2ZnCl_4$ aq.

ETHENYL-(α)-AMIDO-(β)-NAPHTHOL $C_{10}H_6<\substack{N\\O}>C.CH_3$. Formed by heating acetyl-(α)-amido-(β)-naphthol $C_{10}H_6(NHAc)OH$.—$B'_2H_2Cl_2PtCl_4$ 2aq: yellow crystalline powder (Böttcher, *B.* 16, 1939; *C. C.* 1884, 898).

ETHENYL-(α)-AMIDO-NAPHTHYL-MERCAPTAN $C_{10}H_6<\substack{N\\S}>C.CH_3$. [95°] (J.). Formed, together with dicarbyl-amido-naphthyl mercaptan, by heating acetyl-(α)-naphthylamine with sulphur (Hofmann, *B.* 20, 1800). Obtained by oxidation of the thioacetyl derivative of (α)-naphthylamine $C_{10}H_7.N:C(SH).CH_3$ with potassium ferricyanide; the yield is 50 p.c. of theoretical (Jacobsen, *B.* 20, 1898). Colourless prismatic crystals (from alcohol) (J.). Insol. water; volatile with steam (H.). Gives phthalic acid when oxidised by $KMnO_4$ (Jacobsen, *B.* 21, 2624).

ETHENYL-AMIDO-PHENOL *v.* AMIDO-PHENOL, vol. i. p. 170.

ETHENYL-AMIDO-PHENYL MERCAPTAN C_8H_7NS *i.e.* $C_6H_4<\substack{N\\S}>C.CH_3$. (239°).

Formation.—1. By heating *o*-amido-phenyl mercaptan with aldehyde, acetic anhydride, acetonitrile, or acetyl chloride (Hofmann, *B.* 13, 21, 1286).—2. By oxidation of a cold dilute solution of thio-acetanilide in an excess of aqueous NaOH by means of K_3FeCy_6; the yield is 33 p.c. (Jacobsen, *B.* 19, 1072).

Properties.—Colourless oil.

When an alkylo-iodide of this base is mixed with an alkylo-iodide of methenyl-*o*-amido-phenyl mercaptan, and the aqueous solution boiled with NH_3, colouring-matters are obtained analogous to the cyamines (*v.* METHENYL-*o*-AMIDO-PHENYL-MERCAPTAN). In this and other respects the base shows considerable analogy with methyl-quinoline (Hofmann, *B.* 20, 2262). Phthalic anhydride and $ZnCl_2$ at 190° give rise to the compound $C_6H_4<\substack{N\\S}>C.CH:(C_2O_2):C_6H_4$ [above 320°] (Jacobsen, *B.* 21, 2624).

Salt.—$B'_2H_2PtCl_6$: needles or prisms.

ETHENYL-TRI-AMIDO-TOLUENE $C_6H_2(CH_3)(NH_2)<\substack{NH\\N}>C.CH_3$ [1:5:3:4]. [c. 100°].

Preparation.—Di-nitro-acetyl-*p*-toluidine (1 pt.) is reduced with tin (5 pts.) and conc. HCl (10 pts.) and boiled for five or six hours; on concentration of the solution the hydrochloride crystallises out.

Properties.—Transparent monoclinic crystals (containing aq), $a:b:c = 1{\cdot}5813:1:0{\cdot}8216$. V. sol. hot water and alcohol, sl. sol. ether and benzene, nearly insol. cold water.

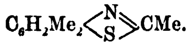
Acetyl derivative $C_6H_2Me(NHAc).N_2HC_2H_3$: [166°]; white concentric needles. Formed by the action of acetic anhydride upon ethenyl-tri-amido-toluene, or upon *p*-acetyl-tri-amido-toluene. By boiling with conc. HCl it is converted into ethenyl-tri-amido-toluene (Niementowski, *B.* 19, 719).

ETHENYL-AMIDO-TOLYL MERCAPTAN $C_6H_3(CH_3)<\substack{N\\S}>C.CH_3$. Prepared by heating *p*-amido-*m*-tolyl mercaptan with acetic anhydride.—$(B'HCl)_2PtCl_4$ (Hess, *B.* 14, 493).

ETHENYL-AMIDOXIM $C_2H_6N_2O$ *i.e.* $CH_3.C(NH_2):NOH$. *Acetamidoxim.* [135°]. Long, pointed crystals. V. sol. water and alcohol. Fe_2Cl_6 gives a deep-red colour. On warming with water it decomposes into hydroxylamine and acetamide. The hydrochloride (B'HCl) is prepared by the action of hydroxylamine on acetonitrile in aqueous alcoholic solution at 30°–40°. It crystallises in white glistening scales [140°]; v. sol. water and alcohol, insol. ether, benzene, and ligroïn. With $NaNO_2$ it yields acetamide and N_2O. With $CuSO_4$ and NH_3 it gives a bluish-green pp. of the formula $C_2H_5N_2OCu(OH)$.

Benzyl ether $CH_3.C(NH_2):N(OCH_2Ph)$: yellow oily liquid; v. sol. alcohol, ether and benzene, nearly insol. water. Its hydrochloride (B'HCl) forms silky white scales [163°], v. sol. water and alcohol (Nordmann, *B.* 17, 2746).

ETHENYL - AMIDO - XYLYL - MERCAPTAN



$C_6H_2Me_2<\substack{N\\S}>CMe$. Oil. From thio-acetyl-xylidine and alkaline K_3FeCy_6 (Gudeman, *B.* 21, 2549).

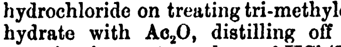
ETHENYL-AZOXIM *v.* Azoxims.

ETHENYL-BROMO-(αβ)-NAPHTHYLENE-DIAMINE *v.* Bromo-ethenyl-naphthylene-diamine.

TRI-ETHENYL-BUTYRIC ACID *v.* Deconoic acid.

ETHENYL TRICARBOXYLIC ACID *v.* Ethane tricarboxylic acid.

ETHENYL - TRI - METHYLENE - DIAMINE



$C_5H_{10}N_2$ *i.e.* $CH_2<\substack{CH_2.NH\\CH_2.N}>CMe$. Obtained as hydrochloride on treating tri-methylene-diamine hydrate with Ac_2O, distilling off HOAc and warming in an atmosphere of HCl (Hofmann, *B.* 21, 2336). The base is a brown oil.

Salts.—$B'_2H_2PtCl_6$: large rhombic crystals, v. sol. water.—$B'HCl.AuCl_3$: needles.

ETHENYL - (1:2) - NAPHTHYLENE - DIAMINE

$C_{10}H_6<\substack{NH\\N}>C.CH_3$. *Naphthylene-acetamidine.* Formed by reduction of the acetyl derivative of (1:2)-nitro-(α)-naphthylamine with tin and HCl (Lellmann a. Remy, *B.* 19, 799). Formed also by reducing bromo-ethenyl-naphthylene-diamine [229°] in alcoholic solution by sodium amalgam (Prager, *B.* 18, 2161), and by reducing acetyl-nitro-(β)-naphthylamine with $SnCl_2$ (Jacobsen, *B.* 14, 1794).

Salts.—B'HCl: small soluble colourless needles. -$B'_2H_2Cl_2PtCl_4$: yellow crystalline pp.—$B'H_2SO_4$:[269°]; white powder.—$B'C_6H_2(NO_2)_3OH$: [242°]; small yellow needles or plates.

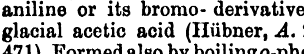
ETHENYL-TRI-PHENOL *v.* Tri-oxy-tri-phenyl-ethane.

ETHENYL-DI-PHENYL-AMIDINE *v.* Di-phenyl-acetamidine.

ETHENYL-PHENYL-AMIDOXIM $CH_3.C(NHPh):NOH$. *Ethenyl-anilidoxim.* [121°]. Formed by heating ethenyl-amidoxim with aniline (Nordmann, *B.* 17, 2752). Large yellow glistening plates. Sol. alcohol, ether, benzene, and hot water, nearly insol. cold water. Fe_2Cl_6 colours it deep-violet to olive-green.

· **ETHENYL-DI-PHENYL-DIAMINE** *v.* Di-phenyl-acetamidine.

ETHENYL-PHENYLENE DIAMINE



$C_8H_8N_2$ *i.e.* $C_6H_4<\substack{NH\\N}>C.CH_3$. [170°] (H.); [175°] (L.). Formed by reducing acetyl-*o*-nitro-aniline or its bromo- derivative with zinc and glacial acetic acid (Hübner, *A.* 209, 352; *B.* 8, 471). Formed also by boiling *o*-phenylene-diamine with glacial acetic acid (Ladenburg, *B.* 8, 677), Needles or leaflets. — The hydrochloride, sulphate and nitrate form colourless needles. —$B''HCl$, $B''H_2SO_4$, $B''_2H_2SO_4$ and $B''HNO_3$.—$B''_2H_2PtCl_6\,x$aq.

Ethenyl-phenylene-diamine carboxylic acid *v.* Ethenyl-di-amido-benzoic acid.

ETHENYL-PROPYLENE DIAMINE

$C_3H_6<\substack{N\\NH}>CMe$. From di-acetyl-propylene-diamine by heating a current of dry HCl (Hofmann, *B.* 21, 2332). — $B'_2H_2PtCl_6$: trimetric crystals, extremely sol. water.—$B'HAuCl_4$: small needles.

ETHENYL-TRI-SULPHONIC ACID *v.* Ethane-tri-sulphonic acid.

ETHENYL-TOLYLENE-*o*-DIAMINE

$C_6H_3Me<\substack{NH\\N}>C.CH_3$. [199°]. Formed with elimination of AcOEt and H_2O, by heating tolylene-*o*-diamine with aceto-acetic ether (Ladenburg a. Rugheimer, *B.* 12, 951; Witt, *B.* 19, 2977). It gives a nitro- derivative [202°].

ETHER $C_4H_{10}O$ *i.e.* Et_2O. *Di-ethyl oxide. Ethyl ether. Sulphuric ether.* [-117°] (Olszewsky, *M.* 5, 128). Mol. w. 74. (34·6°) (Schiff, *A.* 220, 332). S.G. $\frac{20}{4}$ ·7157 (Brühl); $\frac{15}{15}$ ·7201; $\frac{25}{25}$ ·7099 (Perkin, *C. J.* 45, 474). S. 8·3 at 17·5°. S.V. 106·4 (Ramsay); 106·24 (S.); 106·1 (P.). C.E. (0°–10°) ·00152 (Dobriner, *A.* 243, 20). M.M. 4·777 at 20° (P.). μ_β 1·3572 (B.; *cf.* Oudemans jun. *R. T. C.* 4, 269). R_∞ 35·53 (B.). H.F.p. 70,040 (*Th.*); 53,000 (Berthelot). H.F.v. 67,430 (*Th.*).

Critical temperature 194° (Ramsay a. Young, *Pr.* 40, 381; *P. M.* [5] 24, 196).

Effect of dissolved substances on the vapour pressure of ether: Raoult, *C. R.* 104, 976.

Coefficient of Compressibility ·000183 at 21·5° (Isambert, *C. R.* 105, 375).

Formation.—1. From alcohol by treatment with H_2SO_4 (Valerius Cordius, A.D. 1540; Frobenius; Valentin Rose, *Scher. J.* 4, 253; Saussure, *A. Ch.* 89, 273; Dumas a. Boullay, *A. Ch.* [2] 36, 294). Formed also from alcohol by treatment with phosphoric acid (Boullay, *A. Ch.* 62, 192), with arsenic acid (Boullay, *A. Ch.* 78, 284), with BF_3 (Desfosses, *A. Ch.* [2] 16, 72), with $ZnCl_2$ (Masson, *A.* 31, 63) or with $SnCl_4$ (Kuhlmann, *A.* 33, 97, 192).—2. By the action of ethyl iodide (bromide, or chloride) on sodium (or potassium) ethylate (Williamson, *C. J.* 4, 106).—3. From EtI and dry Ag_2O.—4. By heating alcohol with EtBr or EtI at 200° (Reynoso, *A. Ch.* [3] 48, 385).—5. By heating EtBr or EtI with water at 150°-200° (R.).—6. By heating alcohol with HCl, HBr, HI, or chlorides of Mn, Co, Ni, Cd, Zn, Sn, Fe'', Hg'', Ca, Sr, &c. In the case of $CaCl_2$ a temperature of 300° is required (Berthelot, *A.* 83, 104). HgI_2 and SiF_4 also etherify (R.).—7. Alcohol is also etherified by heating with the sulphates of Mg, Zn, Cd, Fe'', Co, Al, and with alums (Reynoso).—8. By heating EtI with Na_2O at 180° (Greene, *C. R.* 86, 1141).—9. By heating alcohol with Et_2SO_4 (Erlenmeyer, *A.* 142, 373).

Preparation.—A mixture of alcohol of 90 p.c. (5 pts.) and conc. H_2SO_4 (9 pts.) is boiled, and alcohol (30 pts.) is allowed to run in continuously through a tube, dipping under the surface of the liquid at such a rate that the liquid boils constantly at 140° (Boullay, *J. Ph.* 1, 97). The distillate separates into two layers, the upper consisting of ether containing alcohol and water in solution, the lower of water containing alcohol and ether in solution; but towards the latter part of the distillation, when the sulphuric acid has become weaker, more alcohol passes over unchanged, and the separation of the ether no longer takes place. The ether is freed from sulphurous and acetic acids by agitation with milk of lime, and is finally rectified. The yield is about 90 p.c. of the theoretical. The amount of olefiant gas formed during the process may be very greatly diminished by keeping the mixture at 130° instead of 140° (Soubeiran, *J. Ph.* [3] 16, 321). Ether may be freed from traces of alcohol and water by fused calcium chloride; or it may be shaken several times with water, and finally dried over quicklime.

Properties.—Colourless, very mobile liquid, with characteristic odour and burning taste. Very inflammable, burning with a luminous flame; its vapour forms an explosive mixture with air. When inhaled it produces insensibility. 35 pts. of ether dissolve 1 pt. of water. It mixes with alcohol, CS_2, chloroform, acetone, and many essential oils; in the latter case presence of water or alcohol is indicated by turbidity (Blanchet, *A.* 7, 157). Wet ether gives turbidity with CS_2. It dissolves iodine and bromine and small quantities of sulphur and phosphorus. It also dissolves $AuCl_3$, Fe_2Cl_6, $HgCl_2$, $Hg(NO_3)_2$, fats, resins, and many other organic bodies. Strong aqueous HCl dissolves ether with evolution of heat, apparently forming an unstable compound. By rapidly evaporating wet ether Tanret (*C. R.* 86, 765) obtained a cryohydrate $C_4H_{10}O$ 2aq [−3·5°].

Reactions.—1. The vapour of ether passed through a *red-hot tube* produces C_2H_4, water, CO, and aldehyde.—2. When a mixture of ether-vapour and air comes in contact with *platinum black*, heated *platinum-sponge*, or other bodies heated not quite to redness, it undergoes slow and imperfect combustion, emitting a pale light, and forming aldehyde, acetic, and formic acids, CO_2, water, &c. Oxidised by a red-hot platinum spiral it gives formic acid, acetic acid, aldehyde, acetal, formic aldehyde and trimetric prisms of $C_{11}H_{33}O_{21}$ [51°]. These prisms are soluble in water, alcohol, ether, or chloroform, and are decomposed by alkalis into formic aldehyde and formic acid. The compound liberates I from KI solution, and reduces PbO_2, and appears, therefore, to be a derivative of H_2O_2 (Legler, *A.* 217, 381).—3. Dry ozonised oxygen acts violently, forming acetic acid, oxalic acid, H_2O_2, and a little formic acid (A. W. Wright, *Am. S.* [3] 7, 184). According to Berthelot (*Bl.* [2] 36, 72) syrupy Et_2O_2 is formed in this reaction.—4. *Sulphuric acid* at 120° forms ethyl-sulphuric acid $EtHSO_4$. When ether is boiled with sulphuric acid the temperature rises from 130° to 180°; SO_2 and Et_2SO_4 pass over while isethionic acid, ethionic acid, &c., remain in the retort.—5. The product of the action of SO_3 separates into an aqueous and a brown ethereal layer. The former contains ethionic acid, which, on boiling, changes to isethionic acid. The latter consists of di-ethyl sulphate (84 p.c.), ethyl ethionate (12 p.c.), and ethyl methionate $CH_2(SO_3Et)_2$ (4 p.c.) (R. Hübner, *A.* 223, 207). The reaction may perhaps be represented as follows:—

$Et_2O + SO_3 = SO_2(OEt)_2$;

$SO_2(OEt)_2 + 3SO_3 =$
$HO.SO_2.O.C_2H_4.SO_2.OH + SO_3H.CH{:}CH.SO_3H$;

$SO_2(OEt)_2 + 2SO_3$
$= HO.SO_2.OEt + SO_3H.CH{:}CH.SO_3H$;

$SO_3H.CH{:}CH.SO_3H + H_2O$
$= SO_3H.CH_2.CH_2O.SO_3H$;

$SO_3H.CH_2.CH_2O.SO_3H + 2SO_3$
$= CH_2(SO_3H)_2 + 2SO_2 + CO_2 + H_2O$.

6. Hot *nitric acid* forms CO_2, acetic acid, and oxalic acid. CrO_3 also oxidises it to acetic acid.—7. HCl gas forms ethyl chloride.—8. Dry *chlorine* forms di-, tetra-, and deca-, chloro-di-ethyl oxides, aldehyde, chloral, EtCl, &c. In presence of water acetic acid and other products of oxidation are formed.—9. A solution of *bromine* in ether becomes colourless after a few days, EtBr, bromal, and other products being formed. According to Schützenberger (*C. R.* 75, 1511) a mixture of bromine and ether deposits in a freezing mixture crystals of $(Et_2O)_2Br_6$ [c. 22°]. Iodine acts but slightly on ether.—10. *Sodium* does not act on pure ether.—11. Heated *soda-lime* forms Na_2CO_3, hydrogen, and CH_4.—12. Red-hot *zinc-dust* forms C_2H_4, water, and hydrogen (Jahn, *M.* 1, 675).

Combinations.—Et_2OSnCl_4: volatile plates, sol. ether, decomposed by water (Kuhlmann, *A.* 33, 106, 192; Lewy, *J. pr.* 36, 146).—$SnBr_4Et_2O$.—Et_2OSbCl_3: [69°]; crystalline hygroscopic powder, sol. alcohol and ether, decomposed by water and by fusion (Williams, *B.* 9, 1135).—$SbBr_3Et_2O$.—$SbBr_32Et_2O$ (Ničklès, *C. R.* 52, 396).—$BiBr_3Et_2O$ 2aq: deliquescent prisms.—Et_2OAsBr_3.—Et_2OTiCl_4. [42°–46°]. (119°). Decomposed by water (Bedson, *C. J.* 29, 309).—$(Et_2O)_3(TiCl_4)_2$ (B.).—$(Et_2O)_2(PCl_5)_3$. White plates, formed by dissolving PCl_5 in dry ether. Violently decomposed by water, giving ethyl-phosphoric acid, but no ether (Liebermann a. Landshoff, *B.* 13, 690).—$BeCl_22Et_2O$ (Atterberg, *B.* 9, 856).—$HgBr_23Et_2O$ (Ničklès, *C. R.* 52, 869).—$Al_2Br_62Et_2O$.—$TlCl_3Et_2OHCl$ aq.—$TlBr_31\frac{1}{2}Et_2O$ (Ničklès, *C. R.* 58, 537).—$VdOCl_3Et_2O$. [below 20°]. Lustrous green crystals (Bedson, *C. J.* 29, 309).

Hydroiodide $(Et_2O)_2HI$. An oil formed by direct combination of ether and HI (Messinger a. Engels, *B.* 21, 327). Insol. ether. Decomposed by KOH into ether and KI, and by water into ether, HI, and EtI.

Hydrobromide $(Et_2O)_2HBr$. Oil. Similar to the hydroiodide.

References.—AMIDO-, BROMO-, and CHLORO-, DI-ETHYL OXIDE.

ETHERIFICATION. The formation of ethers. In the most general sense etherification means the displacement by an alkyl of hydrogen attached to oxygen (or to a halogen in the case of HCl, HBr, and HI). In the narrowest sense it is applied to the making of common ether. The reactions underlying the continuous manufacture of ether may be taken as typical of all cases of etherification. Alcohol was at one time regarded as the hydrate of ether, so that in the manufacture of ether the sulphuric acid merely abstracted a molecule of water from each molecule of ether. It was pointed out by Mitscherlich that ether and water distil over in equivalent proportions (4 pts. of ether to 1 pt. of water), so that the sulphuric acid must be supposed first to take the water from the alcohol and then to give it up again. Mitscherlich and Berzelius therefore said that the sulphuric acid acted 'catalytically.' Liebig (*A.* 23, 39; 30, 129) then pointed out that on mixing alcohol and sulphuric acid hydrogen ethyl sulphate is formed, but on distilling the mixture the quantity of hydrogen ethyl sulphate constantly diminishes as the ether passes over, and he concluded that the hydrogen ethyl sulphate must take part in the formation of ether. He assumed the first reaction to consist in the formation of hydrogen ethyl sulphate from alcohol and sulphuric acid, and that at 120°-140° that body was split up into ether, hydrogen sulphate, and SO_3, the SO_3 then uniting with the water formed in the first reaction. When, however, hydrogen ethyl sulphate is heated alone it gives alcohol and not ether, although, when heated with alcohol, it does give ether. Williamson (*C. J.* 4, 106, 229; *A.* 77, 37; 81, 73; *A. Ch.* [3] 40, 98), while adopting the first of Liebig's equations, showed that the second reaction consisted in the decomposition of hydrogen ethyl sulphate by alcohol. At the same time, Williamson doubled the formula then ascribed to ether for several reasons:

(1) To bring it in accordance with Avogadro's Law.

(2) The difference between the boiling-points of alcohol and of ether (44°) is exactly that usually found between an acid and its ethyl salt.

(3) By the same methods used in preparing ordinary ether it is possible to prepare mixed ethers, such as methyl ethyl oxide MeOEt, and the boiling-points of these ethers are intermediate between those of the two corresponding simple ethers.

(4) There are other reasons for doubling the atomic weight of oxygen.

The two equations proposed by Williamson, and now universally adopted, are

(1) $EtOH + H_2SO_4 = EtHSO_4 + H_2O$
(2) $EtHSO_4 + EtOH = Et_2O + H_2SO_4$.

That ether is alcohol in which an atom of hydrogen has been displaced by ethyl would appear probable from its formation according to the equations

$$EtOH + K = EtOK + H$$
$$EtOK + EtI = EtOEt + KI \text{ (Williamson).}$$

The etherification of an acid by means of alcohol and H_2SO_4 probably takes place for the most part according to such equations as

$$EtOH + H_2SO_4 = EtHSO_4 + H_2O$$
$$EtHSO_4 + HOAc = EtOAc + H_2SO_4.$$

Etherification by alcohol and HCl being represented thus:

$$EtOH + HCl = EtCl + H_2O$$
$$2EtCl + C_4H_6O_4 = Et_2C_4H_4O_4 + 2HCl.$$

ETHERS. Ethers may be simple, mixed, or compound. Simple ethers are oxides of monovalent alkyls; the oxides of divalent radicles, such as ethylene, are not usually classed as ethers. A mixed oxide of two monovalent alkyls, such as MeOEt, is called a mixed ether. A compound ether (or ester) is a hydrogen salt in which the typical hydrogen has been displaced by an alkyl, and may therefore be regarded as an alkyl salt of an acid.

Properties of simple and mixed ethers. The simple and mixed ethers in general resemble ordinary ether in their properties. They are insol. water, and are not decomposed by ammonia, alkalis, sodium, dilute acids, P_2O_5, or cold PCl_5. Conc. H_2SO_4 and SO_3 decompose them (*v.* ETHER). Nitric acid oxidises them to the acids corresponding to the alkyls. If one of the alkyls is benzyl, this becomes benzoic aldehyde (Errera, *G.* 17, 193). HI forms an alcohol and an alkyl iodide; if one of the alkyls is methyl, the iodide is methyl iodide (Silva, *C. R.* 81, 323). Aluminium and iodine produce alkyl iodide, and aluminium iodoalkylate (Gladstone a. Tribe, *C. J.* 30, 357). Chlorine produces products of substitution.

Formation of compound ethers. When an alcohol is heated with an equivalent quantity of an acid, a reaction such as:

$$EtOH + HOAc = EtOAc + H_2O$$

occurs; but as soon as the products of the reaction are formed they begin to react in an inverse sense:

$$EtOAc + H_2O = EtOH + HOAc.$$

Thus, these two reactions occurring simultaneously an equilibrium is ultimately set up (Berthelot a. Péan de Saint-Gilles, *C. R.* 53, 474; 55, 39, 210, 324; 85, 883; *A. Ch.* [3] 68, 225). When molecular mixtures of glacial acetic acid and alcohols are heated to 154° the percentage of acid etherified at the end of the first hour is called by Menschutkin the initial velocity of etherification, while the percentage etherified at the end of 120 hours is called the final limit of etherification.

The initial velocity is 55·6 for methyl alcohol, 46·7 for ethyl, propyl, and *n*-butyl alcohols, 44·9 for isobutyl alcohol, 36·1 for allyl alcohol, 38·0 for benzyl alcohol, 26·5 for isopropyl alcohol, 22·6 for *sec*-butyl alcohol, 10·6 for di-allyl carbinol, 1·4 for *tert*-butyl alcohol, and 1·5 for phenol. It will be seen that the initial velocity is greatest for primary and least for tertiary alcohols, while unsaturated alcohols etherify more slowly than saturated alcohols.

The final limit is 69·6 for methyl alcohol, about 66·8 for ethyl, propyl, butyl, and isobutyl alcohols, about 60 for allyl, benzyl, and *sec*-butyl alcohols, 10 for di-allyl carbinol, and 8·6 for phenol. The limit therefore follows in the main the same variation as the initial velocity, although in the case of primary and secondary alcohols the changes are less marked.

When the rate of etherification of various acids by the same alcohol (isobutyl alcohol was used) is examined it is found that the limit is fairly constant at 67 to 74, while the initial velocity varies from 44·4 for acetic acid to 3·5 for di-methyl-ethyl-acetic acid. Here also the normal compounds show greatest rapidity of etherification. Formic acid shows a greater initial velocity (61·7) and a lower limit (64) than any other organic acid (Menschutkin, *Bl.* [2] 34, 87). In the etherification of alcohols by Ac_2O the greatest velocity is shown by methyl alcohol, but in most cases the reaction is ultimately complete (Menschutkin, *C. R.* 105, 1016; *v.* vol. i. p. 737).

Preparation of compound ethers.—1. Volatile ethers are prepared by distilling a mixture of the alcohol, the acid (or a salt of the acid), and H_2SO_4.—2. Non-volatile ethers are prepared by passing HCl into a solution of the acid in alcohol.—3. The ethers may be prepared by treating the silver salt of the acid with ethyl iodide, and this reaction may be resorted to when neither of the preceding is available.—4. By distilling the potassium salt of an acid with potassium alkyl sulphate.—5. By treating the alcohol with the chloride or anhydride of the acid.—6. By the action of HCl or H_2SO_4 on a solution of the nitrile in an alcohol (Beckurts a. Otto, *C. C.* 1877, 5).—7. According to Veiel (*A.* 148, 160) compound ethers are formed by the oxidation of fatty acids by MnO_2 and dilute sulphuric acid. Thus, butyric acid is said to give propyl butyrate.

Properties of compound ethers.—The compound ethers are almost all insol. water, but are partially saponified by heating therewith; they are saponified by heating with alkalis or alkaline earths, and by HCl or dilute H_2SO_4. Ammonia splits up compound ethers derived from organic acids into the amide and an alcohol. When a compound ether is heated with an alcohol an interchange of alkyls may take place; thus, ethyl acetate and amyl alcohol yield amyl acetate, ethyl amyl oxide, and water (Friedel a. Crafts, *A.* 130, 198; 131, 55). Compound ethers are split up by heating with dry HBr at 100°, forming alkyl bromide and free acid (Gal, *C. R.* 59, 1049). Aluminium and iodine react upon compound ethers of the fatty series, forming an alkyl iodide and aluminium salt (Gladstone a. Tribe, *C. J.* 30, 357). Compound ethers unite with titanium chloride, forming such compounds as $EtOAc(TiCl_4)_2$, $EtOAcTiCl_4$, and $(EtOAc)_2TiCl_4$ (Demarçay, *Bl.* [2] 20, 127; *C. R.* 76, 1414).

Acid ethers. When in polyhydric acids a part only of the typical hydrogen has been displaced by alkyls the resulting acid ether is usually very soluble in water, and readily saponified by boiling therewith.

References.—The particular characters of each group of compound ethers may be gathered by reference to the articles on the ethyl salts of the acids, *e.g.* Ethyl bromide, Ethyl chloride, Ethyl perchlorate, Ethyl iodide, Ethyl nitrate, Ethyl nitrite, Di-ethyl selenide, Ethyl silicate, Ethyl sulphate, Di-ethyl sulphide, Ethyl sulphite, Ethyl thiosulphate, &c.

ETHINE or **ETHINENE** *v.* Acetylene.

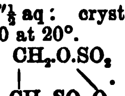
ETHINE-DI-PHTHALYL *v.* Di-phthalyl-ethane.

ETHIONIC ACID $C_2H_6S_2O_7$ *i.e.* $SO_3H.CH_2.CH_2.O.SO_3H$.

Formation.—1. By saturating anhydrous alcohol or ether with SO_3 and diluting with water (Magnus, *P.* 27, 378; 47, 514; Marchand, *P.* 32, 466).—2. Its mono-chloride is formed along with $ClSO_2.OEt$ by action of $ClSO_2OH$ upon ethylene: (a) $Cl.SO_2OH + C_2H_4 = Cl.SO_2OC_2H_5$; and then follows (b) $Cl.SO_2.OH + ClSO_2OEt = HCl + C_2H_4(SO_2.OH)(O.SO_2Cl)$ (Claesson, *J.pr.* [2] 19, 255).—3. From Et_2SO_4 and SO_3 (Hübner, *A.* 223, 208).—4. By the action of H_2SO_4 on isethionic acid $SO_3H.CH_2.CH_2OH$ in the cold (Erlenmeyer a. Carl, *N. Rep. Pharm.* 23, 428).

Properties.—Only known in solution, for on evaporation it splits up into H_2SO_4 and isethionic acid.

Salts.—$K_2A''\frac{1}{2}$ aq: crystalline.—Na_2A''aq.—BaA''aq. S. 10 at 20°.

Anhydride  $\begin{matrix} CH_2.O.SO_2 \\ | \qquad \diagdown \\ CH_2.SO_2.O \end{matrix}$. [80°]. ***Carbyl sulphate.*** Obtained by direct union of ethylene with SO_3; formed also by exposing alcohol to the vapour of SO_3 (Regnault, *A. Ch.* 65, 98; Magnus, *P.* 47, 509). Deliquescent crystals; dissolves in water forming ethionic acid.

Isethionic acid *v.* Isethionic acid.

DIETHOXALIC ACID *v.* Oxy-hexoic acid.

ETHOXY- COMPOUNDS *v.* the ethyl ethers of Oxy- compounds.

ETHOXY-OXALYL CHLORIDE *v.* Chloro-glyoxylic ether.

ETHYL. The radicle C_2H_5 or $CH_3.CH_2$. The ethyl derivatives of hydroxylic compounds are described under the compounds from which they are derived.

Di-ethyl *v.* Butane.

DI-ETHYL-ACETAL *v.* Acetal.

DI-ETHYL-ACETAMIDINE $C_6H_{14}N_2$ *i.e.* $CH_3.C(NHEt):NEt$. (c. 167°). From ethyl-acetamide and PCl_5 the resulting oily base $C_6H_{13}ClN_2$ being subsequently warmed with solid KOH (Wallach a. Hoffmann, *B.* 8, 313; *A.* 184, 108). Syrup, miscible with water, alcohol and ether. Strongly alkaline. Precipitates most metallic salts and dissolves recently ppd. alumina. Boiling alkalis split it up into acetic acid and ethylamine.

ETHYL-ACETAMIDE *v.* *Acetyl*-Ethyl-amine.

ETHYL-ACETANILIDE *v.* *Acetyl*-Ethyl-aniline.

ETHYL ACETATE *v.* vol. i. p. 14.

DI-ETHYL-ACETIC ACID *v.* Hexoic acid.

Ethyl-diacetic acid *v.* ethyl aceto-acetate, vol. i. p. 17.

ETHYL-ACETO-ACETIC ACID *v.* vol. i. p. 23.

ETHYL-DIACETONAMINE *v.* vol. i. p. 28.

ETHYL-ACETO-NITRANILIDE *v.* *Acetyl*-Nitro-ethyl-aniline.

DI-ETHYL-ACETOPHENONE *v.* Phenyl amyl ketone.

ETHYL-ACETO-PROPIONIC ACID *v.* β-Acetyl-*u*-*iso*-valeric acid.

ETHYL - ACETO - SUCCINIC ETHER *v.* Acetyl-ethyl-succinic ether.

ETHYL - DI - ACETYL - ACETIC ETHER *v.* vol. i. p. 23.

ETHYL-ACETYL-ACETONE *v.* Di-methyl propylene diketone.

DI-ETHYL-ACETYL-ACETONE *v.* Di-methyl amylene diketone.

ETHYL-ACETYLENE *v.* Butinene.

ETHYL-ACETYLENE-TETRA-CARBOXYLIC ACID *v.* Butane tetra-carboxylic ether.

ETHYL-ÆSCULETIC ACID *v.* *Ethyl derivative of* Æsculetic acid.

ETHYL ALCOHOL *v.* Alcohol. Derivatives are described as Bromo-ethyl alcohol, Chloro-ethyl alcohol, &c.

TRI-ETHYL-ALCAMINE *v.* Oxy-tri-ethyl-amine.

ETHYL ALDEHYDE *v.* Aldehyde.

ETHYL-ALLYL *v.* Amylene.

TETRA-ETHYL-ALLYL-ALCINE *v.* Tetra-ethyl-oxy-propylene-diamine.

ETHYL-ALLYL-AMINE $(C_2H_5)(C_3H_5)NH$. (85°). Colourless ammoniacal liquid. Miscible with water. Prepared by the action of ethyl iodide on allylamine.

Salts.—B'HCl: small deliquescent plates.—$B'_2H_2Cl_2PtCl_4$: orange needles [c. 155°].—$B'HClPtCl_2$: yellow needles [220°], formed by boiling the preceding salt with water.

—$B'_2H_2SO_4$: tables v. e. sol. water, insol. alcohol and ether. The acid oxalate forms sparingly soluble colourless plates (Rinne, *A.* 168, 261; Liebermann a. Paal, *B.* 16, 525).

Di-ethyl-allyl-amine $(C_2H_5)_2(C_3H_5)N$. (111°). S. 5 at 18°. Colourless liquid. Its aqueous solution becomes turbid on warming. Prepared by the action of ethyl iodide on allyl-amine (Rinne, *A.* 168, 265).

Salts.—$B'_2H_2Cl_2PtCl_4$: large orange crystals [129°].—$B'HClPtCl_2$: yellow needles [189°], formed by boiling the preceding salt with water (Liebermann a. Paal, *B.* 16, 526).—$B'HCl$: very soluble crystals.

Ethylo-bromide $(C_2H_5)_3(C_3H_5)NBr$. *Tri-ethyl-allyl-ammonium bromide.* From triethylamine and allyl bromide (Reboul, *C. R.* 92, 1464). Deliquescent crystals. Split up on distillation into allyl bromide, ethyl bromide, triethylamine, diethylamine, ethylene, *s*-tri-bromo-ethane, and, probably, allylamine. From it may be prepared $(C_2H_5)_3(C_3H_5)NCl$ and the platino-chloride $\{(C_2H_5)_3(C_3H_5)NCl_2\}PtCl_4$, both crystalline.

ETHYL-ALLYL-ANILINE $C_{11}H_{15}N$ *i.e.* $NPhEt(C_3H_5)$. (c. 223°). From allyl-aniline and EtI (Schiff, *A. Suppl.* 3, 364). Thick oil.—$B'C_2H_2O_4$: spherical groups of small needles (from water).

ETHYL-DI-ALLYL-CARBINOL *v.* ENNINYL ALCOHOL.

Di-ethyl-allyl-carbinol *v.* OCTENYL ALCOHOL.

ETHYL-ALLYL-CYANAMIDE $C_6H_{10}N_2$ *i.e.* $CN.NEt(C_3H_5)$. [100°]. From ethyl-allyl-thio-urea, $Pb(OH)_2$, and KOH (Hinterberger, *A.* 83, 348). Needles (from ether). Insol. water, sol. alcohol and ether. Tastes bitter.—$B'_2(HgCl_2)_3$.—$B'_2H_2PtCl_6$.

ETHYL ALLYL OXIDE $C_5H_{10}O$ *i.e.* $C_2H_5.O.C_3H_5$. *Ethyl-allyl ether.* Mol. w. 86. (67°). S.G. $\frac{20}{4}$ ·7651. μ_β 1·3939. $R_\infty = 42{\cdot}2$. *Critical temperature* 245° (Pawlewsky, *B.* 16, 2634). From allyl bromide and NaOEt, allylene being also formed (Brühl, *A.* 200, 178; *cf.* Berthelot a. De Luca, *A. Ch.* [3] 48, 292; Cahours a. Hofmann, *A.* 102, 290). Formed also by treating ethyl di-bromo-allyl oxide $C_2H_5.O.CHBr.CH_2Br$ with sodium amalgam (Markownikoff, *Z.* 1865, 554). Combines with chlorine and bromine, but is not reduced by sodium amalgam. ClOH forms a compound $C_3H_5Cl(OH)(OEt)$ (184°).

ETHYL-ALLYL-THIO-UREA $C_6H_{12}N_2S$ *i.e.* $NHEt.CS.NHC_3H_5$. From allyl thiocarbimide and ethylamine (Hinterberger, *A.* 83, 346; Weltzien, *A.* 94, 103). Syrup.—$B'_2H_2PtCl_6$.—$B'HI$.

Di-ethyl-allyl-thio-urea $C_8H_{16}N_2S$ *i.e.* $NEt_2.CS.NHC_3H_5$. [55°]. Long prisms or needles. V. sol. alcohol and benzene, sl. sol. ligroïn, insol. water. Formed by combination of allyl thiocarbimide and di-ethyl-amine (Gebhardt, *B.* 17, 3038).

ETHYL-ALLYL-UREA $C_6H_{12}N_2O$ *i.e.* $NHEt.CO.NHC_3H_5$. From ethylamine and allyl cyanate. Prisms (Cahours a. Hofmann, *A.* 102, 300).

ETHYL-AMARINE *v.* BENZOIC ALDEHYDE, AMMONIA DERIVATIVES OF.

ETHYL-AMIDO-ACETIC ACID $C_4H_9NO_2$ *i.e.* $NHEt.CH_2.CO_2H$. *Ethyl-glycocoll. Ethyl glycocine.* [above 160°]. Prepared by prolonged boiling of chloro-acetic acid with ethylamine (Heintz, *A.* 129, 27; 132, 1). Indistinct deliquescent laminæ (from alcohol). Sweetish, almost metallic taste. On mixing with an aqueous solution of cyanamide there are deposited long needles of 'ethyl-amido-aceto-cyamidine' $HN{:}C\left\langle\begin{smallmatrix}NH.CO\\NEt.CH_2\end{smallmatrix}\right\rangle$ a homologue of creatinin; S. 9 at 25°; S. (alcohol) 1 at 25° (Duvillier, *C. R.* 103, 211).

Salts.—$HA'HCl$: [c. 180°]; trimetric prisms, v. sol. water and hot alcohol.—$H_2A'_2H_2PtCl_6$ 6aq: large orange-red monoclinic prisms.—$HA'(HgCl_2)_2$: small prisms (from water).—$H_2A'_2HgCl_2$: syrup.—CuA'_2 4aq: prisms, v. sol. water and alcohol, insol. ether.—*Derivative*: DI-CHLORO-ETHYL-AMIDO-ACETIC ETHER (*q.v.*).

Di-ethyl-amido-acetic acid $C_6H_{13}NO_2$ *i.e.* $NEt_2.CH_2.CO_2H$. Obtained by boiling diethylamine with chloro-acetic acid (Heintz, *A.* 140, 217; *Z.* [2] 5, 152). Deliquescent rhombohedral crystals; v. sol. alcohol; sublimes below 100°.—CuA'_2 4aq: small blue prisms.—$H_2A'_2H_2PtCl_6$ aq: orange-red crystals.

Ethyl ether $NEt_2.CH_2.CO_2Et$. (174° uncor.). S.G. $\frac{15}{}$ ·919. From silver-glycocoll and EtI (Kraut, *A.* 182, 172; 210, 317). Alkaline liquid.—$B'_2H_2PtCl_6$: short monoclinic crystals.—$B'_3H_3Bi_2I_9$: slender red needles.

Ethylo-hydroxide. Anhydride. $C_8H_{17}NO_2$ *i.e.* $NEt_3\left\langle\begin{smallmatrix}CH_2\\O\end{smallmatrix}\right\rangle CO$. '*Triethyl glycocoll.*' (210°). Prepared by heating NEt_3 with chloro-acetic ether, boiling the product with baryta water, and heating the resulting ethylo-chloride with silver oxide (Kraut, *A.* 182, 172). Formed also from NEt_3 and chloro-acetic acid (Hofmann, *Pr.* 11, 525; Brühl, *B.* 8, 479; *A.* 177, 201). Deliquescent crystalline mass; partly decomposed by distillation giving off NEt_3.

Ethylo-chloride $NEt_3Cl.CH_2.CO_2H$. From NEt_3 and chloro-acetic acid. Not decomposed by boiling potash or baryta water.

Salts.—$(NEt_3Cl.CH_2.CO_2H)_2PtCl_4$ 2aq: monoclinic prisms.—$(NEt_3Cl.CH_2.CO_2H)AuCl_3$.

Ethylo-iodide $NEt_3I.CH_2.CO_2H$: orange hair-like crystals.—$(NEt_3I.CH_2.CO_2H)_3Bi_2I_6$: orange tables.

Ethylo-nitrate $NEt_3(NO_3).CH_2.CO_2H$: needles, v. e. sol. water.

Ethyl ether of the ethylo-chloride $NEt_3Cl.CH_2.CO_2Et$. From triethylamine and chloro-acetic ether. Needles, v. e. sol. water and alcohol. $(NEt_3Cl.CH_2.CO_2Et)_2PtCl_4$: orange crystals.—$(NEt_3Cl.CH_2.CO_2Et)AuCl_3$: [100°]; needles.

Ethyl ether of the ethylo-iodide $NEt_3I.CH_2.CO_2Et$. From silver glycocoll (3 mols.) and EtI (4 mols.) in the cold.

ETHYL-*o*-AMIDO-ACETOPHENONE $C_6H_4(NHEt).CO.CH_3$. Oil. Obtained by heating *o*-amido-acetophenone with ethyl bromide $B'_2H_2Cl_2PtCl_4$: golden-yellow plates (Baeyer, *B.* 17, 970).

ETHYL-AMIDO-AZO- COMPOUNDS *v.* AZO-COMPOUNDS.

ETHYL-AMIDO-BENZENE *v.* ETHYL-ANILINE.

ETHYL-AMIDO-BENZENE SULPHONIC ACID $NHEt.C_6H_4.SO_3H$. From ethyl-aniline and H_2SO_4 at 200° (Smyth, *B.* 7, 1241).—BaA'_2 2aq.

Di-ethyl-amido-benzene sulphonic acid $NEt_2.C_6H_4.SO_3H$. From di-ethyl-aniline and H_2SO_4 (S.).—BaA'_2 2aq.

ETHYL-*o*-AMIDO-BENZOIC ACID. *Amide* $[2:1]C_6H_4(NHEt).CONH_2$. [129°]. From *o*-amido-benzamide and EtI in alcohol at 100° (Finger, *J. pr.* [2] 37, 441). Crystalline mass, sol. hot water. Gives rise to a nitrosamine $C_6H_4(N(NO)Et).CONH_2$ [110°].

Ethyl-*m*-amido-benzoic acid $C_9H_{11}NO_2$ *i.e.* $[3:1]C_6H_4(NHEt).CO_2H$. [112°]. When potassium *m*-amido-benzoate is boiled with alcoholic EtI a mixture of ethyl- and di-ethyl-amido-benzoic acids is produced; these may be separated by crystallisation of their hydrochloride from hot dilute HCl (Griess, *B.* 5, 1038). Small prisms, sl. sol. hot water, v. e. sol. alcohol and ether. Its solution is tasteless, but acid in reaction. It forms salts with mineral acids but not with HOAc. It gives a nitrosamine $C_6H_4(N(NO)Et).CO_2H$ which crystallises (from water) in yellowish-white long narrow plates, and forms a crystalline silver salt $C_9H_9AgN_2O_3$.

Salts.—HA'HCl: small four- or six-sided plates; also (from dilute HCl) in needles; m. sol. cold, v. sol. hot, water; v. sl. sol. cold HClAq.—BaA'_2 2aq: indistinct plates (from alcohol).

Di-ethyl-*m*-amido-benzoic acid $C_{11}H_{15}NO_2$ *i.e.* $[3:1]C_6H_4(NEt_2).CO_2H$. [90°]. Formed as above (G.). White prisms (containing 2aq); may be distilled.—HA'HCl aq: shining four-sided plates, v. sol. cold water and HClAq.

Di-ethyl-*p*-amido-benzoic acid $[4:1]C_6H_4(NEt_2).CO_2H$. [188°]. From *p*-amido-benzoic acid, KOH, and alcoholic EtI. Also by saponifying its chloride which is obtained by treating di-ethyl-aniline with $COCl_2$ (Michler a. Gradmann, *B.* 9, 1912). Small plates (from alcohol).—$H_2A'_2H_2PtCl_6$.—AgA'.

Ethyl ether EtA'. (315°). Formed, together with the acid, by treating potassium *p*-amido-benzoate with EtI in the cold (Michael a. Wing, *Am.* 7, 198). Oil.

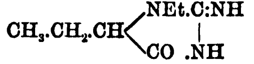
Di-ethyl-di-amido-benzoic acid $C_{11}H_{16}N_2O_2$ *i.e.* $C_6H_3(NEt_2)(NH_2).CO_2H$. From di-ethyl-*m*-amido-benzoic acid by nitration and reduction. Also from benzene-azo-di-ethyl-amido-benzoic acid by reduction (Griess, *B.* 10, 527). Grey needles or prisms (from alcohol).

***p*-DI-ETHYL-AMIDO-BENZOIC ALDEHYDE** $C_6H_4(NEt_2)CHO[1:4]$. [41°]. Needles. Sol. water, alcohol, ether, &c. Formed by the action of alkalis upon di-ethyl-amido-phenyl-tri-chloro-ethyl-alcohol $CCl_3.CH(OH).C_6H_4.NEt_2$, the condensation product of chloral and diethylaniline (Boessneck, *B.* 19, 369).

DI-ETHYL-AMIDO-BENZOPHENONE $C_6H_5CO.C_6H_4NEt_2$. [78°]. *Benzoyl-phenyl-di-ethyl-amine.* From tetra-ethyl-di-amido-tri-phenyl-carbinol and conc. HCl at 180° (Doebner, *A.* 217, 265). Trimetric crystals (from alcohol). Insol. water, sl. sol. cold alcohol, v. sol. hot alcohol. Very feebly basic, dissolving in conc. HCl, but reppd. by water.

Tetra-ethyl-di-amido-benzophenone $CO(C_6H_4NEt_2)_2$. [96°]. Formed, together with $C_6H_3(NEt_2)(CO.C_6H_4NEt_2)_2$ [170°], by saturating di-ethyl-aniline with $COCl_2$, adding half the original volume of di-ethyl-aniline and heating at 120° (Michler a. Gradmann, *B.* 9, 1912). Small laminæ (from alcohol).—$B''H_2PtCl_6$.

ETHYL-*a*-AMIDO-*n*-BUTYRIC ACID $C_6H_{13}NO_2$ *i.e.* $CH_3.CH_2.CH(NHEt).CO_2H$. From *a*-bromo-butyric acid and ethylamine (Duvillier, *A. Ch.* [5] 20, 196; *C. R.* 88, 425; 97, 1486). Crystalline leaflets, subliming above 110° without fusion; v. sol. water, sl. sol. cold alcohol. Mixed with cyanamide in aqueous solution, with addition of a few drops of ammonia, there is formed in a month crystals of di-cyan-di-amide, while from the mother-liquor ethyl-*a*-amido-butyro-cyamide



$CH_3.CH_2.CH\begin{cases}NEt.C{:}NH\\ \quad\quad\ \ | \\ CO\ \ .NH\end{cases}$

may be obtained in tabular crystals, v. sol. water and alcohol.—HA'HCl: opaque, ill-defined, deliquescent crystals.—$H_2A'_2H_2PtCl_6$: orange-red crystals, v. sol. water and alcohol, sl. sol. ether.—$CuA'_2$2aq: blue leaflets.

Di-ethyl-*a*-amido-butyric acid $C_8H_{17}NO_2$ *i.e.* $CH_3.CH_2.CH(NEt_2).CO_2H$. [135°]. From *a*-bromo-butyric acid (1 mol.) and NEt_2H (1 mol.) (Duvillier, *C. R.* 100, 860). Deliquescent crystalline solid, v. sol. water and alcohol, sl. sol. ether. May be distilled with partial decomposition. The cupric salt forms violet-red crystals and dissolves in water and alcohol, forming a violet solution.

ETHYL-AMIDO-CHLORO- *v.* CHLORO-ETHYL-AMIDO-.

ETHYL-*o*-AMIDO-CINNAMIC ACID $C_{11}H_{13}NO_2$ *i.e.* $C_6H_4(NEtH).CH{:}CH.CO_2H$. [125°]. From *o*-amido-cinnamic acid, KOH, EtI, and alcohol by boiling (Fischer a. Kuzel, *A.* 221, 267; *B.* 16, 653; *cf.* Friedländer a. Weinberg, *B.* 15, 1423). Groups of small crystals (from light petroleum). Sl. sol. water, sol. alcohol, ether, and CS_2, forming a yellow solution with green fluorescence.

Nitrosamine $C_6H_4(NEtNO).CH{:}CH.CO_2H$ [150°]. Formed by the action of H_2SO_4 and KNO_2 on the above. Yellowish plates from dilute (25 p.c.) alçohol. Insol. light petroleum, v. sol. ether and chloroform. Insol. acids in the cold. Reduced by zinc and acetic acid to $NH_2.NEt.C_6H_4.CH{:}CH.CO_2H$, which is oxidised by the air to ethyl-quinazole carboxylic acid (Fischer a. Tafel, *A.* 227, 332).

Di-ethyl-*o*-amido-cinnamic acid $C_{13}H_{17}NO_2$ *i.e.* $C_6H_4(NEt_2).CH{:}CH.CO_2H$. [124°]. From amido-cinnamic acid, KOH, alcohol, and EtI (Fischer a. Kuzel, *A.* 221, 269). Pale lemon-coloured plates (from alcohol). Its solutions in alcohol, ether, or CS_2 exhibit bluish-green fluorescence.

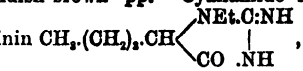
ETHYL-AMIDO-CUMINIC ACID $C_{12}H_{17}NO_2$ *i.e.* $C_{10}H_{11}(NHEt)O_2$. From amido-cuminic acid and EtI at 105° (Lippmann a. Lange, *B.* 13, 1662).—AgA'.

ETHYL-AMIDO-ETHANE SULPHONIC ACID $NHEt.CH_2CH_2.SO_3H$. *Ethyl-taurine.* [147°]. From ethylamine and *β*-chloro-ethane sulphonic acid at 160° (James, *J. pr.* [2] 31, 414). Prisms (from water).

Di-ethyl-amido-ethane sulphonic acid $NEt_2.CH_2CH_2.SO_3H$. [151°]. From diethylamine and $ClCH_2CH_2SO_3H$ (J.). Trimetric tables (from alcohol). V. e. sol. water.

ETHYL-AMIDO-ETHYL ALCOHOL *v.* OXY-TRI-ETHYL-AMINE.

ETHYL-*α*-AMIDO-HEXOIC ACID $C_8H_{17}NO_2$ *i.e.* $CH_3(CH_2)_3CH(NHEt).CO_2H$. S. 10·7 at 15°. From *α*-bromo-hexoic acid and ethylamine (Duvillier, *C. R.* 90, 822; *A. Ch.* [5] 29, 172). Pearly plates (from alcohol). Sl. sol. cold, m. sol. hot, alcohol, insol. ether. Its aqueous solution has a neutral reaction and bitter taste; it gives with Fe_2Cl_6 an intense red colouration, and on boiling a reddish-brown pp. Cyanamide forms the



$$\text{creatinin } CH_3.(CH_2)_2.CH\left\langle\begin{array}{l}NEt.C:NH\\ \qquad\quad |\\ CO\ \ .NH\end{array}\right.$$

, which crystallises in long needles, m. sol. hot water, v. sol. alcohol (Duvillier, *C. R.* 96, 1583).

Salts.—The hydrochloride forms deliquescent laminæ, v. sol. alcohol, insol. ether; the aurochloride is a golden crystalline mass. $(HA'HCl)_2PtCl_4$: orange prisms.—CuA'_2. S. 1 in the cold.

ETHYL-AMIDO-HYDROCARBOSTYRIL *v.* OXY-ETHYL-AMIDO-QUINOLINE DIHYDRIDE.

ETHYL-*o*-AMIDO-HYDROCINNAMIC ACID *v.* ETHYL-*o*-AMIDO-PHENYL-PROPIONIC ACID.

TETRA-ETHYL-DI-AMIDO-METHANE *v.* TETRA-ETHYL-METHYLENE-DIAMINE.

DI-ETHYL-(*a*)-AMIDO-NAPHTHALENE SULPHONIC ACID $NEt_2.C_{10}H_6.SO_3H$. From di-ethyl-naphthylamine and H_2SO_4 (Smith, *C. J.* 41, 184). Needles.—BaA'_2.

DI-ETHYL-AMIDO-NAPHTHOIC ACID $NEt_2.C_{10}H_6.CO_2H$. Di-ethyl-(*a*)-naphthylamine dissolved in benzene is converted by $COCl_2$ into a mixture of two isomeric chlorides of the formula $NEt_2.C_{10}H_6.COCl$ [70°] and [225°] with the compound $NEt_2.C_{10}H_5(CO.C_{10}H_6.NEt_2)_2$ [130°] (Smith, *C. J.* 41, 185).

ETHYL-AMIDO-NAPHTHOQUINONE $C_{10}H_5O_2(NHEt)$. [140°]. From naphthoquinone and ethylamine (Plimpton, *C. J.* 37, 639). Red needles; may be sublimed; v. sol. hot alcohol and benzene, v. sl. sol. ligroïn.

TETRA-ETHYL-DI-AMIDO-DI-NAPHTHYL $C_{28}H_{32}N_2$ *i.e.* $NEt_2.C_{10}H_6.C_{10}H_6.NEt_2$. [190°]. (Much above 360°). Formed by heating di-ethyl-naphthylamine (20 g.) with H_2SO_4 (20 g.) for eight hours at 190°–210°. Crystallises in colourless tufts (from alcohol). Sol. HCl (giving a red solution), strong HNO_3 (intense red colour). V. sol. hot alcohol, m. sol. cold alcohol, sl. sol. ether, v. sol. benzene and $CHCl_3$.

Salt.—B''2(HCl) (B. E. Smith, *C. J.* 41, 182).

***o*-ETHYL-AMIDO-PHENOL** $C_6H_4(NHEt)OH[1:2]$. [168°]. Obtained by heating its ether with fuming HCl for five hours at 150° (Förster, *J. pr.* [2] 21, 350). The product is mixed with NaOH, extracted with ether, the extract dried over $CaCl_2$, and the ether is then boiled off. Trimetric plates. V. sol. alcohol, less sol. benzene, CS_2, chloroform and ether. Cannot be distilled undecomposed.

Salts.—Unstable, decomposing partially when their solutions are evaporated, a resin being formed.—B'HCl.—$(B'HCl)_2PtCl_4$.—B'HBr.

Nitrosamine $C_6H_4(OH)NEt(NO)$. [121°]. Formed by passing nitrous acid gas into a solution of the hydrochloride at 0°. Grey plates. Neither acid nor basic.

Ethyl ether $C_6H_4(NHEt)OEt[1:2]$. (235°). S.G. ^{15} 1·021. Prepared by heating 100 grms. of *o*-amido-phenetol with 84 grms. of EtBr for five hours at 60°. The product is mixed with soda and extracted with ether. The base is dried over $CaCl_2$ and distilled (Förster, *J. pr.* [2] 21, 346). Oil. Gradually turns brown. Miscible with ether, CS_2, chloroform, benzene, and methyl alcohol. Sol. ethyl alcohol. With bleaching powder its solution gives a brown colour. H_2SO_4 and $K_2Cr_2O_7$ give a brown colour. H_2SO_4 dissolves it, forming a reddish-violet solution, the colour being destroyed by water. Nitrous acid gas forms a nitro-nitrosamine $C_6H_3(NO_2)(OEt)NEt(NO)$.

Salts.—B'HBr: trimetric plates.—B'HI: trimetric plates.—B'HCl: trimetric plates.—$(B'HCl)_2PtCl_4$. V. sol. water. Thrown down by fuming HCl.—$B'H_2C_2O_4$. Prisms.

Di-ethyl-*o*-amido-phenol $C_6H_4(NEt_2)(OH)[1:2]$. (220°). Obtained from its ethyl ether by conc. HCl (Förster, *J. pr.* [2] 21, 367).

Properties.—Oil. Turns green in air, but when heated to its boiling-point suddenly loses this colour. When moist it decomposes on distillation. It has a peppery taste, is volatile with steam, and is sol. ether, benzene, chloroform, and alcohol.

Reactions.—1. With Fe_2Cl_6 a deep brownish-red colour.—2. H_2SO_4 and $K_2Cr_2O_7$ a similar colour.—3. Solution of *bleaching powder* gives a wine-red colour.—4. *Bromine water* gives a yellow pp., changing quickly to a brown resin.—5. Conc. H_2SO_4 dissolves it, forming a violet solution.

Salts.—Crystallise very well. The base cannot expel NH_3 from its salts. Solutions of its salts decompose somewhat on evaporating. B'HBr.—B'HCl.—$(B'HCl)_2PtCl_4$.

Ethyl ether $C_6H_4(NEt_2)OEt$ [1:2]. (228°) The ethyl ether of *o*-amido-phenol (2 pts.) and EtI (3 pts.) are heated together in alcoholic solution for twelve hours at 130°; after evaporation the residue is mixed with solution of soda, shaken with ether, and the extract dried over $CaCl_2$ and distilled (Förster). Oil. Miscible with alcohol, ether, benzene, $CHCl_3$ and CS_2. Bleaching-powder solutions give a red colour. H_2SO_4 and $K_2Cr_2O_7$ a reddish-brown colour. Conc. H_2SO_4 forms a violet solution.

Salts.—Glue-like masses. B'HBr.

DI-ETHYL-AMIDO-DIPHENYL $C_{16}H_{19}N$ *i.e.* $C_6H_5.C_6H_4NEt_2$. [below 100°]. From *p*-amido-diphenyl and EtI, followed by Ag_2O (Hofmann, *Pr.* 12, 389). Long white needles; insol. water, m. sol. alcohol, v. sol. ether; may be distilled.—$B'_2H_2PtCl_6$.—B'HBr.—B'HI.

Methylo-iodide $C_6H_5.C_6H_4NEt_2MeI$. Forms crystalline $(C_6H_5.C_6H_4NEt_2MeCl)_2PtCl_4$.

Tetra-ethyl-di-amido-diphenyl $NEt_2.C_6H_4.C_6H_4.NEt_2$. *Tetra-ethyl-benzidine.* [85°]. Formed by heating di-ethyl-aniline with H_2SO_4 to about 200°, and by ethylation of benzidine (Michler a. Pattinson, *B.* 14, 2166). White needles. Sol. alcohol and ether, insol. water. Gives a green colouration with Fe_2Cl_6 or CrO_3.

TETRA-ETHYL-DI-AMIDO-TRI-PHENYL CARBINOL $C_{27}H_{34}N_2O$ *i.e.* $C_6H_5C(OH)(C_6H_4NEt_2)_2$. *Base of 'Brilliant green.'* From di-ethyl-aniline, benzotrichloride and $ZnCl_2$ (Doebner, *A.* 217, 261). Also from di-ethyl-aniline and benzoic aldehyde and oxidation of the product (Fischer, *B.* 14, 2521). Reddish amorphous solid; sl. sol. water, v. sol. alcohol. Its solution in alcohol and in dilute acids is green; in concentrated acids it forms a yellowish-brown solution. Heated with conc. HCl at 180° it forms di-ethyl-aniline and di-ethyl-amido-benzo-phenone: $C_6H_5C(OH)(C_6H_4NEt_2)_2 = C_6H_5.CO.C_6H_4NEt_2 + C_6H_5NEt_2$.

Salts.—Dye a yellower shade than malachite green.—$C_{27}H_{32}N_2H_2SO_4$. Golden crystals. Its solution in alcohol or water is emerald green. — $(C_{27}H_{32}N_2HCl)_2,ZnCl_2$ 2aq. — $B'H_2C_2O_4$ aq: golden prisms.

Leuco-base $C_6H_5CH(C_6H_4NEt_2)_2$. [62°].

ETHYL-AMIDO-PHENYL-CHLORO-ETHYL ALCOHOL *v.* Chloro-ethyl-amido-phenyl-ethyl alcohol.

ETHYL-*o*-AMIDO-PHENYL-ETHANE $C_{10}H_{15}N$ *i.e.* $C_2H_5.C_6H_4.NHEt$. From amido-phenyl-ethane and EtBr (Bernthsen, *A.* 184, 304). Laminæ.—B′HBr: tables.—$B'_2H_2PtCl_6$.

Deca-ethyl-pent-amido-penta-phenyl-ethane $(Et_2N.C_6H_4)_3C.CH(C_6H_4.NEt_2)_2$. [158°]. Obtained by heating 20 pts. of chloral hydrate, 50 pts. of diethylaniline and 10 pts. of $ZnCl_2$ at 100° for five hours. On oxidation it gave a bluish-green dye-stuff (Boessneck, *B.* 19, 367).

TETRA-ETHYL-DI-AMIDO-TRI-PHENYL METHANE $C_6H_5CH(C_6H_4NEt_2)_2$. [62°]. From the carbinol, zinc-dust, and HCl (Doebner, *A.* 217, 263). From di-ethyl-aniline, benzoic aldehyde and $ZnCl_2$. Colourless glassy needles. V. sl. sol. water, v. sol. ether, alcohol, or benzene. $B''H_2Cl_2PtCl_4$ 3aq.

Tetra-ethyl-tri-*ppp*-amido-tri-phenyl-methane $(C_6H_4.NH_2).HC:(C_6H_4.NEt_2)_2$. *Tetra-ethyl-para-leucaniline.* [118°]. Fine concentric needles. Formed by reduction of tetra-ethyl-*p*-di-amido-*p*-nitro-tri-phenyl-methane with zinc-dust and dilute HCl. On oxidation it gives a violet colouring-matter. The acetyl derivative on oxidation yields a green dye-stuff, which dissolves in benzene with a strong fluorescence (Kaeswurm, *B.* 19, 747).

Tetra-ethyl-tri-*ppo*-amido-tri-phenyl-methane $C_6H_4(NH_2).CH(C_6H_4NEt_2)_2$. *o-Amido-leuco-brilliant-green.* [136°]. White needles (containing C_6H_6). Formed by reduction of the condensation product of diethylaniline and *o*-nitro-benzoic aldehyde, by means of zinc-dust and HCl (Fischer a. Schmidt, *B.* 17, 1894).

Hexa-ethyl-tri-amido-tri-phenyl-methane $CH(C_6H_4NEt_2)_3$. Triclinic crystals; $a{:}b{:}c = 1{\cdot}343{:}1{:}?$; $\alpha = 86°\ 9'$; $\beta = 102°\ 38'$; $\gamma = 91°\ 32'$ (Haushofer, *Z. K.* 9, 533).

TETRA-ETHYL-DI-AMIDO-DI-PHENYL-NITRO-PHENYL-METHANE *v.* Nitro-tetra-ethyl-di-amido-tri-phenyl-methane.

TETRA-ETHYL-DI-AMIDO-DI-PHENYL OXIDE $O(C_6H_4NEt_2)_2$. [89°]. From $S(C_6H_4NEt_2)_2$ and silver nitrate (Holzmann, *B.* 21, 2061). Needles, insol. water, sl. sol. cold alcohol and ether.—$B''H_2PtCl_6$. [c. 100°]. Yellow flocculent pp., sl. sol. warm alcohol.—Picrate $B''2C_6H_2(NO_2)_3OH$. [174°]. Yellow crystalline pp., sl. sol. hot alcohol.

Tetra-ethyl-di-amido-di-phenyl peroxide $O_2(C_6H_4.NEt_2)_2$. [67°]. From the corresponding sulphide by treatment with ammoniacal $AgNO_3$ (Holzmann, *B.* 20, 1636). Needles or prisms. Decomposed by moist air.

HEXA-ETHYL-TRI-AMIDO-DI-PHENYL-PHENYLENE DIKETONE $C_{32}H_{41}N_3O_2$ *i.e.* $C_6H_3(NEt_2)(CO.C_6H_4NEt_2)_2$. [c. 170°]. From tetra-ethyl-di-amido-benzophenone, di-ethyl-aniline, and $COCl_2$ at 120° (Michler a. Gradmann, *B.* 9, 1912). Triclinic crystals (from alcohol).

TETRA-ETHYL-DI-AMIDO-DI-PHENYL-PROPANE $CMe_2(C_6H_4NEt_2)_2$. [76°]. Prepared by heating acetone (10 pts.) with diethylaniline (50 pts.) and zinc chloride (30 pts.) in sealed tubes for 12 hours to 170° (Doebner a. Petschow, *A.* 242, 334). Long needles. Insol. water, sl. sol. cold, v. sol. hot, alcohol. Sol. ether, CS_2, petroleum-ether, and benzene.

Salts.—$B''H_2I_2$: reddish yellow pp.; v. sol. hot water and alcohol.

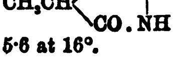
***o*-ETHYL-AMIDO-β-PHENYL-PROPIONIC ACID** $C_6H_4(NHEt)\,CH_2.CH_2.CO_2H$. *Ethyl-amido-hydrocinnamic acid.* From *o*-ethyl-amido-cinnamic acid and sodium amalgam in alkaline solution (Friedländer a. Weinberg, *B.* 15, 2104; Fischer a. Kuzel, *B.* 16, 1449; *A.* 221, 271). Dilute H_2SO_4 throws down the acid as a white flocculent pp., excess of H_2SO_4 dissolves it, and on warming its anhydride oxy-ethyl-quinoline dihydride (ethyl-hydrocarbostyril) separates as an oil.

Nitrosamine $C_6H_4(NEtNO).CH_2.CH_2.CO_2H$. [78°]. Formed by adding $NaNO_2$ to a solution of the acid in H_2SO_4. Groups of colourless oblong plates (from dilute acetic acid). Decomposes at 150°. Sol. alcohol, ether, benzene, and alkalis. Gives Liebermann's reaction. On reduction with zinc-dust and acetic acid it gives $C_6H_4(NEt.NH_2).CH_2.CH_2.CO_2H$, which on evaporating leaves its lactam, ethyl-quinazole dihydride.

TETRA-ETHYL-DI-AMIDO-DI-PHENYL-DI-SULPHIDE $S_2(C_6H_4NEt_2)_2$. [80°]. From di-ethyl-aniline and S_2Cl_2 in ligroïn (Holzmann, *B.* 20, 1636; 21, 2056). Golden prisms; sl. sol. ether, m. sol. alcohol and benzene. Decomposed by water. Forms a crystalline picrate [175°] and platino-chloride.

TRI-ETHYL-TRI-AMIDO-DI-PHENYL-TOLYL CARBINOL $C_{26}H_{33}N_3O$ *i.e.* $C_6H_3Me(NHEt).C(OH)(C_6H_4.NHEt)_2$. *Tri-(?)-ethyl-rosaniline.* From rosaniline (1 pt.), EtI (1 pt.), KOH (1 pt.), and alcohol (Hofmann, *A.* 132, 163).—$C_{26}H_{32}N_3IHI$: lustrous green crystals which form a violet solution in water.

ETHYL-α-AMIDO-PROPIONIC ACID $C_5H_{11}NO_2$ *i.e.* $CH_3.CH(NHEt).CO_2H$. S. 50 at 25°. S. (alcohol) 2 at 25°. Formed by boiling α-bromo-propionic acid with ethylamine (Duvillier, *A. Ch.* [6] 7, 427; *C. R.* 99, 1120; 100, 916). Monoclinic crystals (containing ½ aq) or nacreous plates (from alcohol); sol. water and alcohol. Its hydrochloride forms deliquescent needles. It forms a crystalline platino-chloride and aurochloride.— CuA'_2 2aq: blue prisms, sol. water and alcohol. When its saturated solution is mixed with a solution of cyanamide there is deposited in three months a crystalline homologue of creatinin



$$CH_3CH\begin{cases} NEt.C{:}NH \\ \quad\quad | \\ CO\,.\,NH \end{cases}$$

; S. 27 at 17°; S. (alcohol) 5·6 at 16°.

ETHYL-AMIDO-ISOPROPYL ALCOHOL *v.* Ethyl-oxy-isopropyl-amine.

DI-ETHYL-AMIDO-PROPYLENE-GLYCOL *v.* Di-ethyl-di-oxy-propyl-amine.

ETHYL-AMIDO-TOLUENE *v.* Amido-tolyl-ethane and Ethyl-toluidine.

Ethyl-tri-amido-toluene $C_9H_{15}N_3$ *i.e.* $C_6H_2Me(NHEt)(NH_2)_2$ [1:4:3:5]. Obtained by reducing di-nitro-*p*-tolyl-ethyl-nitramine with tin and HCl (Van Romburgh, *R. T. C.* 3, 412).

a-**ETHYL-AMIDO-ISOVALERIC ACID** $C_7H_{15}NO_2$ *i.e.* $(CH_3)_2CH.CH(NHEt).CO_2H$. From bromo-isovaleric acid and ethylamine (Duvillier, *A. Ch.* [5] 21, 439; *C. R.* 88, 425). Groups of slender white needles; sol. water and alcohol, insol. ether. Neutral to litmus. Sublimes above 110°.—HA'HCl: confusedly crystalline; v. sol. water and alcohol, insol. ether.—CuA'_2xaq: crystalline violet mass forming an intense blue solution.—The platinochloride and aurochloride are exceedingly deliquescent.

ETHYLAMINE C_2H_7N *i.e.* NH_2Et. Mol. w. 45. (19°). S.G. $^{\underline{8}}$ ·6964. V.D. 1·5767. H.F.p. 17,510. H.F.v. 15,770 (*Th.*).

Compressibility: Isambert, *C. R.* 105, 1173.

Formation.—1. By boiling cyanic or cyanuric ether with potash (Wurtz, *C. R.* 28, 223, 323; *A. Ch.* [3] 30, 443).—2. Together with NH_3 by boiling ethyl-urea with potash (W.).—3. By the action of ammonia on the ethers of inorganic acids, *e.g.*: EtBr and EtI (Hofmann, *C. J.* 13, 331), EtCl (Groves, *C. J.* 13, 331), Et_3PO_4 (De Clermont, *A. Ch.* [3] 44, 335), Et_2SO_4 (Strecker, *A.* 75, 46), $EtNO_3$ (Juncadella, *C. R.* 48, 332), $KEtSO_4$ (Erlenmeyer a. Carl, *J.* 1875, 617), and Et_2SO_3 (Carius, *A.* 110, 209).—4. By heating chloride, bromide, or iodide of ammonium with alcohol or ether in sealed tubes (Berthelot, *A. Ch.* [3] 38, 63).—5. Formed, together with di- and tri-ethyl-amine, by heating absolute alcohol with ammoniacal $ZnCl_2$ at 260°; the yield of mixed bases amounts to about 46 p.c. of the alcohol used (Merz a. Gasiorowski, *B.* 17, 637).—6. From propionitrile, zinc, and dilute H_2SO_4 (Mendius, *A.* 121, 142).—7. By the dry distillation of alanine (Limpricht a. Schwanert, *A.* 101, 297). Occurs also among the products of the dry distillation of beet-root molasses (Duvillier a. Buisine, *A. Ch.* [5] 23, 317).—8. Occurs among the products of the putrefaction of yeast and flour (Hesse, *J. pr.* 71, 471; Sullivan, *J.* 1858, 231).—9. With di- and tri-ethyl-amine by heating white precipitate NH_2HgCl with EtI (Sonnenschein, *A.* 101, 20). 10. By heating acetamide with alcoholic sodium-ethylate at 170°–200° (Seifert, *B.* 18, 1357).—11. By the action of alkalis on propionic bromo-amide, or of bromine and KOH on propionamide; yield 80 p.c. of theoretical (Hofmann, *B.* 15, 753).—12. By reduction of a cold solution of aldehyde-phenyl-hydrazide in 5 pts. of alcohol by means of sodium-amalgam (2 p.c.) and acetic acid; yield 45 p.c. of the theoretical. $B'_2H_2Cl_2PtCl_4$: hexagonal prisms (Tafel, *B.* 19, 1926).

Preparation.—1. Cyanic ether is boiled with aqueous KOH, the escaping gas is absorbed by HClAq, and the ethylamine hydrochloride dried, mixed with quick-lime, and distilled (Wurtz). The potassium cyanate from which the cyanic ether is prepared (by distillation with $KEtSO_4$) is usually sufficiently impure to give off NH_3, which then produces all three ethylamines, so that the product is seldom quite pure.—2. Ethyl nitrate is heated with alcoholic ammonia. NH_4Cl is hardly soluble in alcohol, and the ethyl-amines are separated by crystallisation of their picrates (Carey Lea, *C. N.* 5, 118).—3. A mixture of propionamide (1 mol.) and bromine (1 mol.) is treated in the cold with a 5 p.c. solution of KOH, and the solution run slowly into a 30 p.c. solution of (3 mols. of) KOH at 60°–70° as described under methylamine; the yield is 80–90 p.c. (Hofmann, *B.* 15, 767).—4. EtBr is heated with conc. NH_3Aq in sealed tubes at 100° (Hofmann, *C. J.* 3, 300).—5. EtI is heated with aqueous NH_3 at 100°. The product is distilled with KOH. The mixture of the three ethylamines is dried over KOH and mixed with oxalic ether. Ethylamine forms diethyl-oxamide NHEt.CO.CO.NHEt, di-ethyl-amine forms di-ethyl-oxamic ether $NEt_2.CO.CO.CO_2Et$, whilst the tri-ethyl-amine has no action, and is removed by distillation. The liquid di-ethyl-oxamic ether is then separated by filtration from the crystalline di-ethyl-oxamide. On distilling the di-ethyl-oxamide with potash ethylamine passes over. EtCl obtained as a by-product in the manufacture of chloral may be used instead of EtI in the above preparation (Hofmann, *B.* 3, 109, 776). When EtCl is heated in equimolecular proportions with conc. NH_3Aq at 90° a floating layer of tri-ethyl-amine containing free NH_3 is formed, while ethylamine and diethylamine remain dissolved as salts, and constitute the chief product. The same mixture of EtCl and NH_3Aq when heated at 150° forms NH_4Cl, ethylamine hydrochloride, and NEt_4Cl as chief products, only traces of $NHEt_2$ and of NEt_3 (free) being formed (Malbot, *A. Ch.* [6] 13, 477; *C. R.* 105, 755).—6. A good modification of the preceding method, proposed by Groves (*C. J.* 13, 331), consists in heating ethyl chloride (1 mol.) with a solution of ammonia (1 mol.) in alcohol. After removing the insoluble ammonium chloride the alcohol is distilled off, and the hydrochlorides are decomposed by soda. The bases are received in water, sulphuric acid added, and the solution of the sulphates evaporated to a syrup. This is poured into absolute alcohol, in which ammonium sulphate is insoluble (*cf.* Wanklyn a. Chapman, *Pr.* 15, 218). The sulphates are again decomposed, and the bases received in water, and to the solution ethyl oxalate is added, in a quantity calculated on the supposition that the alkalinity is due to mono-ethyl-amine. The separated diethyl oxamide is filtered off and the syrupy mother liquor is boiled for 12 hours with 10 times its volume of water, so as to form acid diethylamine oxalate and di-ethyl-oxamic acid. On concentration the former salt separates out in long needles, and on decomposition yields pure diethylamine. The molten liquor is decomposed with soda, the separated bases received in alcohol and again treated with ethyl oxalate, and the mixture distilled to remove the triethyl-amine and alcohol, and to the residue milk of lime is added to precipitate calcium mono- and di- ethyl-oxamate, which on decomposition yield diethylamine (Duvillier a. Buisine, *A. Ch.* [5] 23, 340; *C. R.* 88, 31).

Properties.—Colourless inflammable liquid;

does not solidify at −140°. Possesses a pungent ammoniacal odour, a strong alkaline reaction, and burning taste, inflaming the tongue. It forms dense white fumes with HCl. It mixes with water, considerable rise of temperature taking place, but it is completely expelled again by boiling. Solid KOH separates it from its aqueous solution. It expels NH_3 from ammonium salts. An aqueous solution of ethylamine resembles one of NH_3 in behaviour towards many metallic salts; it differs in dissolving the ppd. oxides of aluminium, gold, and ruthenium, and in not dissolving the pps. which it gives with salts of Cd, Ni, and Co. It dissolves ppd. cupric hydroxide less readily than NH_3 does. With $SnCl_4$ it gives a pp. very soluble in excess. Phosphomolybdic acid gives a yellow pp. more soluble than the corresponding pp. obtained with ammonia. An alcoholic solution of chloro-tri-nitro-benzene (picryl chloride) gives the characteristic ethyl-picramide $C_6H_2(NO_2)_3(NHEt)$ with even small quantities of ethylamine (Van Romburgh, *R. T. C.* 2, 107). A concentrated aqueous solution of ethylamine that has been dehydrated as far as possible by KOH yields on distillation dry ethylamine gas, followed very soon by a liquid boiling below 75°, which is probably a hydrate of ethylamine (Wallach, *B.* 7, 326). From an examination of the compressibility of a solution of ethylamine in water, Isambert also concludes that chemical combination does take place between the water and the base (Isambert, *C. R.* 105, 1173).

Reactions.—1. On passing through a *red-hot tube* there is formed NH_3, hydrogen, HCy, CH_4, C_2H_2, C_6H_6, C_2H_4, and carbon (Muller, *Bl.* [2] 45, 438).—2. *Nitrous acid* produces nitrogen and alcohol (or nitrous ether).—3. *Chromic acid mixture* oxidises it to aldehyde, acetic acid, water, and nitrogen (Wanklyn a. Chapman, *C. J.* 20, 328).—4. *Cyanic acid* forms ethyl-urea.—5. *Cyanic ether* gives di-ethyl-urea.—6. *o-Oxy-benzoic aldehyde* forms syrupy $C_9H_{11}NO$ (237°), sol. water (Dennstedt a. Zimmermann, *B.* 21, 1553).—7. Dry ethylamine hydrochloride is converted by $COCl_2$ into NHEt.COCl at 260° (Gattermann a. Schmidt, *B.* 20, 118).—8. *Allyl thiocarbimide* (oil of mustard) gives ethyl-allyl-thio-urea (Hinterberger, *A.* 83, 346).—9. Gaseous *cyanogen chloride* forms ethyl-cyanamide, which is converted by boiling water into the isomeric iso-tri-ethyl-melamine (Hofmann, *B.* 2, 602; Cloez a. Cannizzaro, *A.* 78, 228).—10. *Bleaching-powder* gives ethyl-di-chloro-amine (Tcherniak, *B.* 9, 143).—11. *Di-chloro-naphthoquinone* forms $NHEt.C_{10}H_4ClO_2$ [110°].—12. *Benzoic aldehyde* in aqueous or alcoholic solution forms benzylidene-ethyl-amine PhCH:NEt (195°), an oil which is reduced by sodium-amalgam to benzyl-ethyl-amine $PhCH_2NHEt$ (Zaunschirm, *A.* 245, 279). 13. SO_3 forms ethyl sulphamic acid $NHEt.SO_3H$.

Salts.—The sulphate, chloride, tartrate, and other salts differ from the corresponding ammonium salts in being very much more soluble in alcohol.—$B'HCl$ [76°-80°]. Mol. w. 81½. R_∞ 35·11 in an 11 p.c. aqueous solution (Kanonnikoff). Large deliquescent laminæ (from alcohol) or striated prisms (from water). On distillation it gives ethyl-amine, di-ethyl-amine, EtCl, C_2H_4, and NH_3 (Fileti a. Piccini, *B.* 12, 1508).—$B'_2H_2PtCl_6$: orange hexagonal rhombohedra. S.G. $\frac{19\cdot1}{4}$ 2·253 (Clarke, *Am.* 2, 175). Not decomposed by boiling water (De Coninck, *Bl.* [2] 45, 131).—$B'HAuCl_4$: very slender golden monoclinic prisms, sol. water, alcohol, and ether (Wurtz).—$B'_2H_2HgCl_4$: small white scales (from alcohol).—$B'HHgCl_3$: deliquescent trimetric crystals (Köhler, *B.* 12, 2211, 2324; Topsoë, *Z. K.* 8, 246).—$B'HHg_5Cl_{11}$: hexagonal rhombohedra.—$B'HClHgCy_2$: large laminæ, permanent in the air, decomposed at 100°; sol. water, sl. sol. cold alcohol (Kohl a. Swoboda, *A.* 83, 342).—$B'_2H_2PdCl_4$: feathery tufts of large black crystals; red by transmitted light (Reckenschuss, *A.* 83, 343; *cf.* Müller, *A.* 86, 366).—$B'_2H_2CuCl_4$: trimetric crystals.—$B'HBr$: crystalline.—$B'_2H_2SO_4$×: deliquescent gummy mass, v. sol. alcohol.—$B'HNO_3$×: very deliquescent thin laminæ.—$MgB'HPO_4$ 5aq: bulky pp. obtained by adding sodium phosphate to a solution of magnesium sulphate mixed with ethylamine or any of its salts; becomes crystalline on standing.—$B'_2H_2Mo_2O_7$: white scales, becoming brown on drying (Meyer, *J. pr.* 67, 151).—$B'_2H_2SO_4Al_2(SO_4)_3$ 24aq: S. 15 at 25°; regular octahedra (Stenner a. Kanmer, *A.* 91, 172).—$B'H_2CO_3$(?): very unstable crystalline mass obtained from $B'HCl$ and Na_2CO_3.—$B'HOAc$×: deliquescent crystalline mass.—$B'H_2S$: crystals; vapour-tension 48 at 13° (Isambert, *C. R.* 96, 708).—$B'HVO_3$ (Bailey, *C. J.* 45, 692).—$B'_4(H_2O)_2(V_2O_5)_3$ 3aq.—$B'_2H_2O(V_2O_5)_2$: red prisms (Ditte, *C. R.* 104, 1844).—$B'HCyS$: deliquescent; not converted into ethyl-thio-urea at 150° (De Clermont, *Bl.* [2] 27, 198).—$B'H_2C_2O_4$: trimetric laminæ (Loschmidt, *Sitz. W.* 51 [2] 7, 384; *J.* 1865, 376).—$B'_2H_2C_2O_4$: monoclinic crystals.—Camphorate $B'_2C_{10}H_{16}O_4$: small needles (Wallach a. Kamensky, *A.* 214, 242).—Mucate $B'_2C_6H_{10}O_8$ 8aq: oblique rhombic prisms (Bell, *B.* 10, 1861).—Pimelate $B'_2C_7H_{12}O_4$ (Wallach a. Kamensky, *B.* 14, 170).—Benzene sulphonate $C_6H_5SO_3HB'$ [92°] (Norton a. Westenhoff, *Am.* 10, 129).—*p*-Toluene sulphonate $B'HSO_3.C_6H_4Me$ [111°] (Norton a. Otten, *Am.* 10, 140).—Combinations with salts.—$B'HgCl_2$: crystalline pp. got by mixing alcoholic solutions of ethylamine and $HgCl_2$ (Köhler, *B.* 12, 2208, 2323).—$B'_2HgCl_2Hg_2O_2$: pp. got by mixing the aqueous solutions. By boiling with excess of $HgCl_2$ there is formed an insoluble yellow salt NHEt.HgClHgO, while crystalline NHEt.HgCl remains in solution.—B'_2PtCl_2: fawn-coloured powder.—B'_4PtCl_2 2aq: colourless crystals, v. sol. water.—B'_4PtSO_4.—$B'_2(NH_3)_2PtCl_2$ (Gordon, *B.* 3, 174).—$B'C_2H_4PtCl_2$ (Martius a. Griess, *A.* 120, 326).

Formyl derivative NHEt.CHO. (197°). S.G. ^{21} ·952. Mixes with water, alcohol, and ether.

Acetyl derivative C_4H_9NO *i.e.* NHAcEt. (202°) S.G. $^{4\cdot5}$ ·942. Formed by the action of ethylamine on acetic ether; or of HOAc on cyanic ether (Wurtz, *A. Ch.* [3] 30, 491; *C. R.* 37, 180). Colourless liquid. Formed also by dehydrating ethylamine acetate. PCl_5 converts it into $C_8H_{15}ClN_2$ whence solid KOH forms, on warming, di-ethyl-acetamidine $C_6H_{14}N_2$ (Wallach a. Hoffmann, *B.* 8, 1567; *A.* 184, 108).

Di-acetyl derivative $C_6H_{11}NO_2$ *i.e.* $NEtAc_2$. (185°-192°). S.G. ^{22} 1·009. From cyanic ether and Ac_2O at 190° (Wurtz, *A. Ch.* [3] 42, 43). Liquid.

Valeryl derivative $CMe_3.CO.NHEt$. [49°]. (204°). Crystals; v. sol. water, alcohol, and ether; has no smell. Pure HNO_3 attacks it slowly, giving off N_2O (Franchimont a. Klobbie, *R. T. C.* 6, 241).

Heptoyl derivative $C_6H_{13}.CO.NHEt$. [6°]. (268°). Formed by heating ethylamine heptoate to 230° (F. a. K.). Pure HNO_3 gives off N_2O.

Benzoyl derivative $C_6H_5.CO.NHEt$: [67°]; (260°); glistening needles (from water) or plates (from dilute alcohol). From ethylamine and BzCl (Romburgh, *R. T. C.* 4, 390). Formed also by the action of ethyl-carbamic chloride OC(NHEt)Cl upon benzene in presence of Al_2Cl_6 (Gattermann a. Schmidt, *B.* 20, 120; *A.* 244, 50).

o-Amido-benzoyl derivative $C_6H_4(NH_2)CO.NHEt$. [105°]. From isatoic acid and ethylamine (Finger, *J. pr.* [2] 37, 437). White colloid mass; sol. alcohol and hot ligroin. HNO_2 converts it into $C_6H_4\Big<{}^{CO}_{N_2}\Big>NEt$. [70°].

Ethyl-chloro-amine NHEtCl. *Acetyl-derivative* NAcEtCl. Formed by passing chlorine into NAcEtH at −18° (Norton a. Tcherniak, *C. R.* 86, 1409). Liquid, v. sol. water, alcohol, and ether; decomposed by heat. Boiling soda-solution decomposes it into chloroform, ethyl-di-chloro-amine, ethyl carbamine and NH_2Et.

Ethyl-bromo-amine. *Acetyl derivative.* NAcEtBr. From acetyl-ethylamine by warming with a solution of bromine in aqueous KBr (N. a. T.).

Ethyl-di-chloro-amine NCl_2Et. (89°). S.G. $\frac{0}{0}$ 1·240; $\frac{15}{15}$ 1·230. Obtained by chlorinating ethylamine at 0° (Wurtz, *A. Ch.* [3] 30, 474). Prepared also by distilling ethylamine hydrochloride (100 g.) with bleaching-powder (250 g.) made into a thick cream with water (Tcherniak, *B.* 9, 146). Pungent yellow oil; not solid at −30°. Insol. acids. Decomposes spontaneously in damp air into NH_4Cl, ethylamine hydrochloride, chloroform, acetyl chloride, and acetonitrile. Reduced to NH_2Et by H_2S. Alkalis give HOAc and NH_3. Converts aniline into di- and tri-chloro-aniline, being itself reduced to NH_2Et (Pierson a. Heumann, *B.* 16, 1047). Reacts with $ZnEt_2$ diluted with ether with formation of ethylamine and tri-ethylamine (Köhler, *B.* 12, 770, 1869).

Ethyl-di-iodo-amine NI_2Et. From ethylamine and iodine (Wurtz; Raschig, *A.* 230, 221). Dark red pp.

Diethylamine $C_4H_{11}N$ *i.e.* $NHEt_2$. Mol. w. 73. (56°). S.G. ^{0} ·726; ^{10} ·716; ^{20} ·706; $^{\underline{50}}$ ·674 (Oudemans, *R. T. C.* 1, 56). S. V. 109 (Schiff). H.F.p. 29,320 (*Th.*), 31,100 (M.). H.F.v. 26,420 (*Th.*). H.C. 724,400 (gaseous); 716,900 (liquid) (Müller, *Bl.* [2] 44, 609).

Formation.—1. By heating ethylamine with EtBr (Hofmann, *T.* 1850, 120; *C. J.* 3, 300).—2. By heating ammonia with EtCl, EtBr, or EtI as described under ethylamine.—3. Together with ethylamine by heating ethyl nitrate with ammonia (Carey Lea, *J. pr.* 86, 176).—4. Together with mono- and tri-ethyl-amine by heating absolute alcohol with ammoniacal $ZnCl_2$ at 260° (Merz a. Gasiorowski, *B.* 17, 637).

Preparation.—1. By treating its nitrosamine with conc. HClAq (Geuther, *Jenaische Zeitschr.* 7, 118).—2. By acting on di-nitro-di-ethylaniline $C_6H_3(NO_2)_2NEt_2$ with dilute KOH, the other product being $C_6H_3(NO_2)_2OK$. The yield is good (Van Romburgh, *R. T. C.* 2, 35).—3. *v.* ETHYLAMINE.

Properties.—Volatile inflammable liquid with strong alkaline reaction; v. sol. water. It differs from ethylamine in not redissolving the pp. which it forms with zinc salts, in not ppg. a solution of $PdCl_2$, and in the fact that the pp. which it forms with $HgCl_2$ is not soluble in acetic acid, whereas the pps. formed by ethylamine and by NH_3 are soluble in HOAc.

Reactions.—1. When passed through a *red-hot tube* it forms HCy, NH_3, carbon, CH_4, hydrogen, C_2H_2, benzene, and nitrogen, but no ethylene (Muller, *Bl.* [2] 45, 438).—2. *Iodine* forms an oily substitution product.—3. *Potassium nitrite* converts its hydrochloride into di-ethyl-nitrosamine NEt_2NO. This is a neutral yellowish oil, (177°), S.G. $^{\underline{17\cdot5}}$ ·951, V.D. 3·36 (calc. 3·53) (Geuther a. Kreutzhage, *A.* 127, 43). It is split up by alcoholic KOH at 140° into NH_3 and ethylamine.—4. *Cyanic ether* forms tri-ethyl-urea (Hofmann, *C. R.* 54, 252).—5. *Cyanogen chloride* forms liquid di-ethyl-cyanamide (190°) (Cloez a. Cannizzaro, *A.* 78, 228).—5. SO_3 forms di-ethyl-sulphamic acid NEt_2SO_3H.

Salts.—B′HCl [217°], (320°–330°), non-deliquescent plates (Wallach, *B.* 14, 748). V. e. sol. water, m. sol. alcohol, v. sol. chloroform (Behrend, *A.* 222, 119).—$B'_2H_2PtCl_6$: orange monoclinic crystals (Topsoë, *Z. K.* 8, 246).—$B'HAuCl_4$: trimetric crystals.—$B'HHgCl_3$: trimetric crystals.—$B'HCl(HgCl_2)_5$: hexagonal rhombohedra.—$B'_2H_2Cl_2(HgCl_2)_5$: dimorphous.—$B'_2H_2PtBr_6$: monoclinic.—$B'H_2S$: crystalline; its vapour-pressure is 150 mm. at 10° (Isambert, *C. R.* 96, 708).—$B'HNO_3$. [100°]. Long needles or prisms (Franchimont, *R. T. C.* 2, 338).—$B'H_2C_2O_4$: long needles, m. sol. water (Duvillier a. Buisine, *A. Ch.* [5] 23, 342). Benzene sulphonate $B'HSO_3.C_6H_5$: [139°] (Norton, *Am.* 10, 129).—*p*-Toluene sulphonate $B'HSO_3.C_6H_4Me$: [88°] (N.).

Formyl derivative NEt_2CHO (178°). S.G. $^{\underline{12}}$ ·908. From di-ethyl-oxamic acid by heating (Wallach, *B.* 14, 745). Liquid, miscible with water.—$B'_2H_2PtCl_6$.—$B'_2H_2PtCl_6$2aq. With PCl_5 it forms a base $C_8H_{14}N_2$ (Wallach, *A.* 237, 236).

Acetyl derivative $C_6H_{13}NO$ *i.e.* NEt_2Ac. (186°). S. G. $^{\underline{8\cdot5}}$ ·925 (Wallach a. Kamensky, *A.* 214, 235).

Tri-chloro-acetyl derivative $CCl_3.CO.NEt_2$. [27°] (F. a. K).; [90°] (C.). From $NHEt_2$ and $CCl_3.COCl$ (Franchimont a. Klobbie, *R. T. C.* 6, 236). From hexa-chloro-acetone and $NHEt_2$ (Cloez, *A. Ch.* [6] 9, 145).

Valeryl derivative $CMe_3.CONEt_2$. (203°). S.G. $^{\underline{15}}$ ·891 (F. a. K.).

Heptoyl derivative $C_6H_{13}CO.NEt_2$. [below −15°]. (258°). S. G. $^{\underline{15}}$ ·881 (F. a. K.).

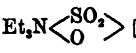
Benzoyl derivative NEt_2Bz. (282°). S.G. $^{\underline{15}}$ 1·019; oil; sol. dilute HCl but reppd.

by water (Hallmann, *B.* 9, 846; Romburgh, *R. T. C.* 4, 387).

Triethylamine $C_6H_{15}N$ *i.e.* NEt_3. Mol. w. 101 (*cf.* Dewar a. Scott, *Pr.* 35, 347). (90°). S.G. $^{20}_{4}$·7277 (Brühl, *A.* 200, 186). S.V. 153·86 (Schiff). μ_β 1·406. R_∞ 53·86. H.F.p. 42,080 (Thomsen); 34,400 (Muller, *Bl.* [2] 44, 609). H.F.v. 38,020 (*Th.*). H.C. 1,047,100 (gaseous); 1,038,300 (liquid) (M.). *Critical temperature*, 267° (Pawlewsky, *B.* 16, 2633).

Formation.—1. By heating diethylamine with EtBr.—2. From cyanic ether and KOEt.—3. By heating ammonia with EtI, EtBr, EtCl, or $EtNO_3$; *v.* ETHYLAMINE (Hofmann, *C. J.* 3, 300; Carey Lea, *C. N.* 6, 142).—4. Together with ethylene and water by the destructive distillation of tetra-ethyl-ammonium hydroxide (Hofmann).—5. Together with mono- and di-ethyl-amine, by heating absolute alcohol with ammoniacal $ZnCl_2$ at 260° (Merz a. Gasiorowski, *B.* 17, 637).

Properties. — Strongly alkaline liquid, inflammable, having an ammoniacal odour; sl. sol. water. Its aqueous solution forms with salts of Zn, Cd, Be, Zr, Ni, Co, Sn'', Ag, Hg'', Cu, Pb, Fe, and Mg, pps. insol. excess; with salts of Al and Sn^{iv} a pp. v. sol. excess; with $AuCl_3$ it gives a yellow pp. insol. excess, which soon blackens from reduction to AuCl, an odour of aldehyde being formed.

Reactions.—1. At a temperature of 1200° it gives HCy, ammonia, carbon, hydrogen, CH_4, acetylene, and C_2H_4, but no benzene or N (Muller, *Bl.* [2] 45, 438).—2. $KMnO_4$ oxidises it, giving CO_2 and HOAc (Wallach a. Claisen, *B.* 8, 1237).—3. Its hydrochloride is not decomposed by aqueous KNO_2 in the cold, but on boiling some $NEt_2.NO$ is formed (Geuther, *Z.* [2] 2, 513).—4. When heated with *a*-bromo-butyric acid and water there is formed *a*-oxy-butyric acid and NEt_3HBr. The same products appear to be formed when no water is present (Duvillier, *Bl.* [2] 48, 3; *cf.* Brühl, *B.* 9, 34).—5. SO_3 forms  $Et_3N{<}^{SO_2}_{O}{>}$ [92°] which crystallises in tables; sol. alcohol, acetone, and hot water; sl. sol. cold water and ether. It is decomposed by boiling water into acid triethylamine sulphate (Beilstein a. Wiegand, *B.* 16, 1267).—6. Triethylamine combines directly with the chlorides, bromides, and iodides of primary alkyls, forming ammonium derivatives that are not decomposed by KOH, but are converted by moist Ag_2O into non-volatile, caustic bases. When the alkyl is secondary or tertiary an olefine and a salt of triethylamine are the chief products. Thus, isopropyl iodide at 100° forms NEt_3HI and C_3H_6, while Me_3CBr forms NEt_3HBr and butylene (Reboul, *C. R.* 93, 69).

Salts. — B'HCl: white, non-deliquescent laminæ.—$B'_2H_2PtCl_6$: orange monoclinic crystals, v. sol. water.—$B'HAuCl_4$: monoclinic crystals.—$B'_2H_2HgCl_4$: hexagonal crystals (Topsoë).—$B'HHg_2Cl_5$: monoclinic. — $B'HHg_5Cl_{11}$: hexagonal rhombohedra.—$B'_2H_2CuCl_4$: monoclinic.—$B'HNO_3$. [99°]. Hygroscopic crystals (Franchimont, *R. T. C.* 2, 338).—$B'H_2PtBr_6$: monoclinic.—$B'HBiI_4$: scarlet prisms (Kraut, *A.* 210, 317).—$B'H_2C_2O_4$: trimetric plates (Loschmidt, *J.* 1865, 375; *Sitz. W.* 51 [2] 7, 384).

Benzene sulphonate $C_6H_5.SO_3HB'$. [121°] (Norton, *Am.* 10, 129).—*p*-**Toluene sulphonate** $C_6H_4Me.SO_3HB'$. [65°] (N.).

Tetra-ethyl-ammonium hydroxide NEt_4OH. Obtained by decomposing its iodide by moist Ag_2O or its sulphate by baryta. Very deliquescent, hair-like needles. Absorbs CO_2 from the air. Strongly alkaline, saponifying fats. Its solution rubbed between the fingers feels like caustic potash; it strongly attacks the tongue, and when dilute has a bitter taste. With metallic solutions it behaves like potash, except that alumina is less soluble in it, and hydrated chromic oxide is quite insoluble. A very concentrated solution, as well as the dry base, is split up at 103° into NEt_3, water, and C_2H_4. Its solution boiled for 24 hours with EtI gives NEt_4I and alcohol.

Salts of Tetraethyl ammonium (Hofmann, *C. J.* 4, 304; *A.* 78, 253).—NEt_4Cl. The union of NEt_3 with EtCl takes place with difficulty in dilute alcoholic solutions (Malbot, *A. Ch.* [6] 13, 545).—$(NEt_4)_2PtCl_6$: orange pp.; sl. sol. water, v. sl. sol. alcohol and ether.—NEt_4AuCl_4: lemon-yellow pp.; sl. sol. cold water and HClAq.—$(NEt_4)_2Hg_5Cl_{12}$: white crystalline pp.; sol. water and boiling HClAq, from which it separates as unctuous plates (Hofmann).—$(NEt_4)_2HgCl_4$: dimetric crystals (Topsoë, *J.* 1883, 620).—NEt_4HgCl_3: triclinic.—$NEt_4Hg_2Cl_5$: triclinic. — $NEt_4Hg_3Cl_7$: monoclinic. — $NEt_4Hg_5Cl_{11}$: hexagonal rhombohedra. — NEt_4Cl_2I: regular crystals deposited from a hot solution of NEt_4Cl and ICl in water (Tilden, *C. J.* 19, 145).—$(NEt_4)_3Bi_2Cl_9$: six-sided tables (Jörgensen, *J. pr.* [2] 3, 344).—$(NEt_4)_2CuCl_4$: dimetric crystals. — NEt_4Br. — NEt_4Br_3 [78°]: light-red pp. or orange-red needles (from alcohol); v. sol. alcohol and CS_2. A solution of iodine in aqueous KI added to its alcoholic solution throws down NEt_4I_3 (Clamor-Marquart, *J. pr.* [2] 1, 429).—NEt_4Br_5: crimson pp.; gives off $\frac{2}{5}$ of its Br in air.—$(NEt_4)_3Bi_2Br_9$ (Jörgensen).—NEt_4I. The union of NEt_3 with EtI takes place slowly in the cold, but when it is started at 100° it goes on with great vigour. Large crystals (from water); v. sol. cold water, sol. alcohol, insol. ether. Decomposed on distillation into NEt_3 and EtI. Not acted on by KOHAq, but less soluble therein than in water. Decomposed by $AgNO_3$, by Ag_2SO_4, or by moist Ag_2O, yielding NEt_4NO_3, $(NEt_4)_2SO_4$, or NEt_4OH respectively.—NEt_4I_3: red needles (Weltzien, *A.* 86, 292; 91, 33).—NEt_4I_7: [108°]; dark-violet plates (Geuther, *A.* 240, 66).—$(NEt_4I)_25HgI_2$: from NEt_4I and HgI_2.—$(NEt_4I)_23HgI_2$: yellow crystals formed by the action of EtI on N_2Hg_3 or NHg_2H_2Cl; m. sol. alcohol, not decomposed by water (R. Müller, *A.* 108, 6; Sonnenschein, *A.* 101, 20).—NEt_4IHgI_2: from NEt_4I_3 and Hg (Risse, *A.* 107, 224).—$C_{32}H_{78}N_4Hg_8I_{18}$: [150°]; from $NH_2.HgCl$ and IEt: golden-yellow crystals, insol. alcohol, ether, and water.—$(NEt_4I)_3Bi_2I_6$ (Jörgensen, *J. pr.* [2] 3, 339).—$(NEt_4)_2W_2O_7$: deliquescent (Classen, *J. pr.* 93, 446). — $(NEt_4)_2Mo_2O_7$ 3aq: deliquescent (C.). — $(NEt_4)_2O6SnO_2$ aq: insoluble dimetric octahedra.—$(NEt_4)_2O7SnO_2$ aq.—$(NEt_4)_2CrO_4$: not crystallised.—$(NEt_4)_2Cr_2O_7$: prisms (C.).—NEt_4AsO_3: crystalline.—$(NEt_4)_4Sb_2O_7$: deliquescent (C.).—**Picrate** [251°] (Lossen, *A.* 181, 375).—$(NEt_4)_3FeCy_6$ 4aq: from Ag_3FeCy_6 and NEt_4I

(Bernheimer, *B.* 12, 409).—NEt_4VO_3 (Bailey, *C. J.* 45, 693).

Tri-ethylamine methylo-hydroxide $NEt_3Me(OH)$. *Methyl-tri-ethyl-ammonium hydroxide. Derivatives*: NEt_3MeI. From NEt_3 and MeI (Hofmann, *A.* 78, 277). V. e. sol. water, but ppd. from its solution by KOH.—NEt_3MeI_5: [16°]; dark green plates.—NEt_3MeI_7: [42°]; brownish-violet plates.—$(NEt_3MeCl)_2PtCl_4$: dimetric crystals.—$NEt_1MeAuCl_4$: dimetric.—$(NEt_3MeCl)_2HgCl_2$: dimetric (Topsoë, *Z. K.* 8, 246).—$(NEt_3MeCl)_4 5HgCl_2$: monoclinic.—$NEt_3MeCl(HgCl_2)_2$: monoclinic crystals.—$(NEt_3MeCl)_2CuCl_2$.—NEt_3MeI_3 (Müller, *A.* 108, 5).—Picrate [268°] (Lossen, *A.* 181, 374).

Tri-ethylamine iodo-methyl-hydroxide. *Derivatives*: $NEt_3(CH_2I)I$. From NEt_3 and CH_2I_2 (Lermontoff, *B.* 7, 1253). Dimetric tables, v. sol. water. Boiling with Ag_2O suspended in water gives $NEt_3(CH_2I)OH$.—$(NEt_3CH_2I)_2PtCl_6$: octahedra.

Tri-ethylamine amylo-hydroxide $NEt_1(C_5H_{11})OH$. Not obtained crystalline. The iodide $NEt_3(C_5H_{11})I$ forms slender unctuous crystals, v. sol. water and alcohol, insol. ether (Hofmann, *C. J.* 4, 313).

DI-ETHYLAMINE DISULPHONIC ACID $C_4H_{11}NS_2O_6$ *i.e.* $NH(CH_2.CH_2.SO_3H)_2$. *Imido-di-ethane disulphonic acid.* Formed by heating taurine with baryta-water at 220° (Salkowsky, *B* 7, 117).

ETHYL-AMMELINES *v. Cyanuric acid* in the article Cyanic acid.

ETHYL-AMYL is Heptane.

DI-ETHYL-AMYL-AMINE $NEt_2(C_5H_{11})$. (154°). Obtained, together with water and ethylene, by the dry distillation of $NEt_4(C_5H_{11})OH$ (Hofmann, *C. J.* 4, 315). Liquid, sol. water.

ETHYL-ISO-AMYL-ANILINE $C_{13}H_{21}N$ *i.e.* $NPhEt(C_5H_{11})$. Mol. w. 191. (262°). From isoamyl-aniline and EtBr; or from ethyl-aniline and isoamyl bromide at 100° (Hofmann, *A.* 74, 156; 79, 13). Liquid. Its hydrobromide is resolved by distillation into ethyl-aniline and isoamyl bromide. HNO_3 and H_2SO_4 give a product [c. 72°] (Van Romburgh, *R. T. C.* 2, 103).—$B'_2H_2PtCl_6$: [100°].

Methylo-iodide $NPhEt(C_5H_{11})MeI$. Moist Ag_2O forms $NPhEt(C_5H_{11})MeOH$, which is resolved by distillation into ethylene, water, and methyl-isoamyl-aniline. Gives the platinochloride $(NPhEt(C_5H_{11})MeCl)_2PtCl_4$.

DI-ETHYL-ISOAMYL BORATE $Et_2(C_5H_{11})BO_3$. (174°). S.G. $^{\underline{26}}$ ·858 (Schiff, *A. Suppl.* 5, 154).

Ethyl-di-isoamyl borate $Et(C_5H_{11})_2BO_3$. (c. 213°). S.G. $^{\underline{0}}$ ·876.

ETHYL ISOAMYL CARBONATE $Et(C_5H_{11})CO_3$. (182° cor.). S.G. $^{\underline{27}}$ ·92 (Röse, *A.* 205, 230). PCl_5 gives $C_5H_{11}O.COCl$ and EtCl.

ETHYL AMYL KETONE $C_2H_5.CO.CEtMe_2$. *Ethyl-amyl-pinacolin.* (151°). S.G. $^{\underline{0}}$ ·845; $^{\underline{21}}$ ·829. From $CEtMe_2.COCl$ and $ZnEt_2$ (Wyschnegradsky, *A.* 178, 107). Formed also by boiling the pinacone $CMeEt(OH).CMeEt(OH)$ with diluted H_2SO_4 (Lavrinovitch, *A.* 185, 126). Gives on oxidation acetic acid and $CEtMe_2.CO_2H$.

Ethyl amyl ketone $C_8H_{16}O$. (154°). S.G. ·841. Occurs among the by-products in the preparation of ether (Hartwig, *J. pr.* [2] 23, 449). Oil, smelling like camphor. Reduces to a secondary alcohol $C_8H_{20}O$. Oxidation gives propionic and valeric acids.

ETHYL ISOAMYL OXIDE $C_7H_{16}O$ *i.e.* $Et.O.C_5H_{11}$. *Ethyl amyl ether.* (112°). V.D. 4·04. S.G. $^{\underline{18}}$ ·764. H.F. 49,000 (Berthelot). Prepared by the action of potassium isoamylate KOC_5H_{11} on EtI; or of potassium ethylate on isoamyl iodide (Williamson, *C. J.* 4, 233). Not formed by distilling a mixture of ethyl and isoamyl alcohols, since amylene is given off (Guthrie, *A.* 105, 37). Oil, lighter than water, smelling like sage.

Ethyl *tert*-amyl oxide $Et.O.CMe_2Et$. (102°). S.G. $^{\underline{0}}$ ·779; $^{\underline{18}}$ ·751. A by-product in the formation of amylene by the action of alcoholic potash on tert-amyl iodide: the yield being 2 p.c. (Kondakoff, *J. R.* 1887, 300: Reboul, *C. R.* 64, 1243).

DI-ETHYL-ISO-AMYL-PHOSPHINE $Et_2(C_5H_{11})P$. (186°). Formed by treating di-ethyl-isoamyl-phosphine hydrochloride with NaHO. A colourless slightly viscid liquid (Collie, *C. J.* 53, 722).

Tri-ethyl-iso-amyl-phosphonium chloride. Formed by heating iso-amyl chloride with tri-ethyl phosphine at 130° in a sealed tube (Collie). Very deliquescent. Decomposed above 300° into ethylene and di-ethyl-isoamyl-phosphine hydrochloride $Et_2(C_5H_{11})PHCl$. The platinochloride forms thick needles. M. sol. water.

TRI-ETHYL-ISOAMYL SILICATE $Et_3(C_5H_{11})SiO_4$. (216°–225°). From isoamyl alcohol and $ClSi(OEt)_3$ (Friedel a. Crafts, *A. Ch.* [4] 9, 5).

Di-ethyl-di-isoamyl silicate $Et_2(C_5H_{11})_2SiO_4$. (245°–250°). S.G. $^{\underline{0}}$ ·915. From $Cl_2Si(OEt)_2$ and isoamyl alcohol.

Ethyl-tri-isoamyl silicate $Et(C_5H_{11})_3SiO_4$ (280°–285°). S.G. $^{\underline{0}}$ ·913. From Cl_3SiOEt and isoamyl alcohol.

ETHYL-ISOAMYL SULPHIDE $C_7H_{16}S$ *i.e.* $Et.S.C_5H_{11}$. (160° i.V.) (B.). S.G. $^{\underline{0}}$ ·852. From $NaSC_5H_{11}$ and EtI; or from $C_5H_{11}I$ and NaSEt in dry alcohol (E. O. Beckmann, *J. pr.* 125, 449; A. Saytzeff, *A.* 139, 361). Colourless oil with alliaceous odour. MeI at 100° gives SMe_3I, ethyl iodide, and $C_5H_{11}I$. HgI_2 forms a compound $HgI_2 2SEt(C_5H_{11})$.

Ethyl-amyl-di-sulphide $(C_2H_5)(C_5H_{11})S_2$. Formed by oxidation of an ethereal solution of ethyl- and amyl-mercaptans with bromine. Thin colourless liquid. Volatile with steam. Lighter than water. Miscible with alcohol and ether, insol. water (Otto a. Rössing, *B.* 19, 3134).

ETHYL-ISO-AMYL SULPHONE $Et(C_5H_{11})SO_2$. [14°]. (270° i.V.). S.G. $^{\underline{18}}$ 1·032. From ethyl-isoamyl sulphoxide (*q. v.*) and aqueous $KMnO_4$ (E. O. Beckmann, *J. pr.* 125, 450).

ETHYL-ISOAMYL SULPHOXIDE $Et(C_5H_{11})SO$. From ethyl-isoamyl sulphide (1 pt.) and (2 pts. of) HNO_3 (S.G. 1·4). Crystalline (Beckmann, *J. pr.* 125, 449). Oil, solidified by a freezing mixture at −16°. May be reduced to ethyl isoamyl sulphide.

ETHYL-ISOAMYL THIOCARBONATE *v. Ethyl thiocarbonate.*

ETHYL-ANHYDRACETONE BENZIL *v.* vol. i. p. 462.

ETHYL-ANILINE $C_8H_{11}N$ *i.e.* NPhEtH. Mol. w. 121. (204°). S.G. $^{\underline{18}}$ ·954. Formed by heating a mixture of aniline with excess of EtBr to boiling; on cooling, a mass of crystals of its hydrobromide is formed (Hofmann, *C. J.* 3, 285). Prepared by saponifying its acetyl derivative with boiling alcoholic KOH; the acetyl derivative may be obtained by warming alcohol (300 g.), acetanilide (75 g.), KOH (31 g.), and EtBr (65 g.); the reaction is at first violent, and the yield of ethyl-aniline is 41 p.c. of the theoretical (Pictet, *B.* 20, 3422; *cf.* Hepp. *B.* 10, 327; Elsbach, *B.* 15, 690). Prepared also by heating aniline hydrochloride with ethyl alcohol (1$\frac{1}{20}$ mol.) for 8 hours at 150°; the yield being 52 p.c. of the theoretical (Reinhardt a. Staedel, *B.* 16, 29). Commercial ethyl-aniline may be purified by fractional treatment with phthalic anhydride (Piutti, *A.* 227, 181).

Properties.—Oil, sol. alcohol, smelling like aniline. Gives no blue colour with bleaching powder solution; colours fir-wood and elder pith less strongly yellow than aniline. Turns brown in air and light.

Reactions.—1. HNO_3 gives off CO_2 and red fumes, but forms also tetra-nitro-ethyl-aniline (Van Romburgh, *R. T. C.* 2, 31).—2. *Nitrous acid* forms the nitrosamine $C_6H_5NEt(NO)$, a heavy yellowish oil, v. sol. alcohol and ether, neutral in reaction, and re-converted into ethyl-aniline by treatment with zinc and dilute H_2SO_4 (Griess, *B.* 7, 218).—3. A solution of acetone saturated with SO_2 forms large crystals of $C_3H_6OSO_2NPhEtH$ (Boessneck, *B.* 21, 1906).—4. Its phenyl-ethyl-phthalamate loses H_2O at 200°, becoming $CO<\begin{matrix}C_6H_4\\O\end{matrix}>C(NPhEt)_2$ (Piutti, *A.* 227, 181).—5. *Cyanogen chloride* forms PhNEtCy (271°) (Cloëz a. Cahours, *A.* 90, 94).

Salts.—B'HBr: large trimetric tables (from alcohol); v. e. sol. water (Hjortdahl, *Z. K.* 6, 473).—$B'_2H_2PtCl_6$: long needles; v. sol. water and alcohol.—$B'HCl^{x}$: crystalline mass; converted at 320° into the hydrochloride of amido-phenyl-ethane $C_6H_4Et.NH_2$ (Hofmann, *B.* 7, 526).—$B'HBrCdBr_2$: trimetric.—$B'_2H_2SnBr_6$: monoclinic.—B'HI: trimetric tables.—Ethyl sulphate $B'HEtSO_4Et_2SO_4$: prisms: from NPhEtH and Et_2SO_4 in benzene (Claesson a. Lundwall, *B.* 13, 1704).

Formyl derivative $C_6H_5NEtCHO$. (260°). S.G. ^{16} 1·063 (Pictet a. Crépieux, *B.* 21, 1106; *cf.* Tobias, *B.* 15, 2866).

Acetyl derivative C_6H_5NAcEt. [55°]. (249°); (258°) at 731 mm. (P. a. C.). From sodium acetanilide and EtI. Also from di-ethyl-aniline and AcBr. Prisms; sol. ether (Elsbach, *B.* 15, 690; Staedel, *B.* 16, 29; 19, 1948).

Benzoyl derivative $C_6H_5.NEtBz$. [60°]; large crystals; v. sol. alcohol, ether, &c., insol. water. Formed by heating di-ethyl-aniline with benzoyl chloride at 200° (Hess, *B.* 18, 687).

Di-ethyl-aniline $C_{10}H_{15}N$ *i.e.* $C_6H_5NEt_2$. Mol. w. 149. (214°). S.G. ^{18} ·936. S.H. ·476 between 8° and 80° (R. Schiff, *G.* 17, 286). Formed by heating ethyl-aniline with excess of EtBr (Hofmann, *A.* 74, 135). Prepared by heating aniline-hydrobromide (or hydroiodide) with (2$\frac{1}{20}$ mols. of) ethyl alcohol to 150° for 8 hours; the yield is 98 p.c. of the theoretical (Reinhardt a. Staedel, *B.* 16, 29).

Properties.—Oil. Gives no colour with bleaching powder. Does not turn brown in air. Benzoyl chloride at 180° forms EtCl and benzoyl-ethyl-aniline (Hess, *B.* 18, 687). AcBr forms EtBr and NPhEtAc (Staedel, *B.* 19, 1948). HNO_3 forms tetra-nitro-ethyl-aniline (Van Romburgh, *R. T. C.* 2, 31). Nitrous acid gives nitroso-di-ethyl-aniline $C_6H_4(NO)NEt_2$, which crystallises from ether in green prisms [84°], and dissolves in dilute acids.

Salts.—B'HBr: four-sided tables; sublimes in needles.—$B'_2H_2PtCl_6$: yellow prisms (from alcohol); less soluble than the platinochloride of ethyl-aniline.—$B'_2H_2Cl_2SnBr_4$: monoclinic prisms (Hjortdahl, *J.* 1882, 524).—$B'_2H_2Br_2SnBr_4$.

Methylo-iodide B'MeI: [102°]; identical with methyl-ethyl-aniline ethylo-iodide. By treatment with KOH it gives methyl-ethyl-aniline (Claus a. Howitz, *B.* 17, 1326). The corresponding hydroxide splits up on distillation into ethylene, water, and di-ethyl-aniline. Its salts are: $(NPhEt_3Cl)_2PtCl_4$.—$NPhEt_3I_3$ [81°]. $NPhEt_3I_5$ [68°] (Dafert, *M.* 4, 502).

Ethylo-iodide $NPhEt_3I$.—$NPhEt_3OH$.—$NPhEt_3Cl$. — $(NPhEt_3Cl)_2PtCl_4$ (Hofmann, *A.* 79, 2).

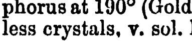
References.—Bromo-, Chloro-, Chloro-nitro-, and Nitro- ethyl-aniline.

ETHYL-ANILINE AZYLINE *v. Di-ethyl-amido-benzene-*Azo-*di-ethyl-aniline.*

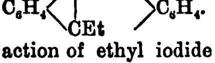
ETHYL-ANILINE SULPHONIC ACID *v.* Ethyl-amido-benzene sulphonic acid.

ETHYL-ANTHRACENE $C_{16}H_{14}$ or $C_6H_4<\begin{matrix}C(C_2H_5)\\CH\end{matrix}>C_6H_4$. [61°]. Large plates. Prepared by reduction of ethyl-oxanthranol with zinc-dust and NH_3 (Liebermann a. Tobias, *B.* 14, 802; *A.* 212, 109). Picric acid compound [120°].

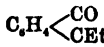
ETHYL-ANTHRACENE-DIHYDRIDE $C_{16}H_{16}$ or $C_6H_4<\begin{matrix}CHEt\\CH_2\end{matrix}>C_6H_4$. (322° cor.). S.G. $\frac{18}{18}$ 1·049. Prepared by reduction of ethyl-oxanthranol with P and HI (S.G. 1·7) (Liebermann, *B.* 13, 1600; *A.* 212, 76). Clear fluorescent liquid. Miscible with alcohol, ether, benzene, and acetic acid in all proportions. Cautious treatment with CrO_3 in glacial acetic acid reconverts it into ethyl-oxanthranol; further oxidation gives anthraquinone.

Di-ethyl-anthracene dihydride  $C_6H_4<\begin{matrix}CEt_2\\CH_2\end{matrix}>C_6H_4$. [50°]. From di-ethyl-anthrone, HIAq (S.G. 1·7), and amorphous phosphorus at 190° (Goldmann, *B.* 21, 1176). Colourless crystals, v. sol. ligroïn, ether, and CS_2. Oxidised by CrO_3 in HOAc to di-ethyl-anthrone.

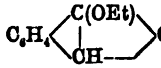
Ethyl-anthracene-hydride-nitrite $C_{14}H_8(C_2H_5)(NO_2)_3$. [130°]. Large crystals. Sol. benzene. Prepared by the action of HNO_3 on an acetic acid solution of ethyl-anthracene-hydride. On oxidation with CrO_3 it gives anthraquinone (Liebermann a. Landshoff, *B.* 14, 473).

ETHYL-ANTHRANOL *Ethyl ether*  $C_6H_4<\begin{matrix}C(OEt)\\|\\CEt\end{matrix}>C_6H_4$. [77°]. Formed by the action of ethyl iodide and KOH on anthranol (Goldmann, *B.* 21, 2506). Needles (from dilute alcohol); v. e. sol. benzene, ether, and petroleum ether. Oxidised by chromic acid to ethyl-oxanthranol $C_6H_4<\begin{matrix}CO\\C(OH)Et\end{matrix}>C_6H_4$ [106°].

DI-ETHYL-ANTHRONE $C_{18}H_{18}O$ *i.e.*



$C_6H_4\left<\begin{matrix}CO\\CEt_2\end{matrix}\right>C_6H_4$. Formed together with the ethyl derivative of anthranol



$C_6H_4\left<\begin{matrix}C(OEt)\\|\\CH\end{matrix}\right>C_6H_4$ by boiling anthranol with conc. KOHAq and EtI (Goldmann, *B.* 21, 1176). [136°]. Colourless crystals, v. sol. benzene, chloroform, alcohol, and ether, sol. ligroïn, insol. aqueous alkalis. Oxidised by CrO_3 in HOAc to anthraquinone. Does not combine with Br. Not affected by HCl in HOAc at 180°.

ETHYL ARSENATE $(C_2H_5)_3AsO_4$. (237°). S.G. $\frac{0}{}$ 1·326. Decomposed by water into alcohol and arsenic acid (Crafts, *Bl.* [2] 14, 99).

ETHYL ARSENITE $(C_2H_5)_3AsO_3$. (166°). S.G. $\frac{0}{4}$ 1·224. Formed from Ag_3AsO_3 and EtI. Prepared by the action of NaOEt on $AsCl_3$ or $AsBr_3$ in alcoholic solution. Only $\frac{3}{4}$ of the calculated quantity of NaOEt is used, to avoid saponification of the ether. Excess of $AsBr_3$ is removed by passing in dry NH_3 and filtering from the pp. Arsenious ether is also formed by heating Et_4SiO_4 with As_2O_3 at 200°. It is not affected by dry NH_3 but is decomposed by water into alcohol and As_2O_3. HBr gives alcohol and $AsBr_3$ (Crafts, *Bl.* [2] 14, 99).

ETHYL-ARSINES *v.* ARSENIC, ORGANIC COMPOUNDS OF.

ETHYLATION OF BASES. The displacement of hydrogen by ethyl in primary and secondary bases is usually effected by heating with ethyl iodide (bromide or chloride), the resulting compound being decomposed by potash. Another method consists in heating the hydrochloride (hydrobromide or hydroiodide) of the base with 10 p.c. more than the calculated quantity of ethyl alcohol at 150° for 8 hrs.; the yield varies from 28 p.c. to 99 p.c. of the theoretical, according to the base. The reaction takes place most readily with the iodide, and least readily with the chloride (*cf.* Reinhart a. Staedel, *B.* 16, 29).

ETHYL-ATROLACTIC ACID *v. Ethyl derivative* of α-OXY-α-PHENYL-PROPIONIC ACID.

ETHYL-ATROPINE *v.* ATROPINE.

ETHYL-AZAUROLIC ACID *v.* AZAUROLIC ACID.

ETHYL-BARBITURIC ACID *v. Ethyl derivative* of BARBITURIC ACID.

ETHYL-BENZENE C_8H_{10} *i.e.* $C_6B_5.C_2H_5$. Mol. w. 106. (136° i. V.). S.G. $\frac{20}{4}$ ·8673 (Brühl, *A.* 235, 12); $\frac{9·9}{4}$ ·8760 (Schiff, *A.* 220, 92). C. E. (9·9° to 135·8°) ·00129. V.D. 3·65 (calc. 3·66). S.V. 138·9. μ_D 1·496. S.H. ·393 at 0° (Schiff, *A.* 234, 300).

Occurrence.—In Dippel's oil (Weidel a. Ciamician, *B.* 13, 70).

Formation.—1. From EtBr, C_6H_5Br and Na (Fittig, *A.* 131, 310; 133, 222; 144, 278).—2. From benzene, Al_2Cl_6, and EtCl or ethylene (Friedel a. Crafts, *A. Ch.* [6] 1, 457; 14, 456; Rennie, *C. J.* 41, 33; Balsohn, *Bl.* [2] 31, 540; Söllscher, *B.* 15, 1680).—3. By heating benzene (4 pts.) with ether (1 pt.) and $ZnCl_2$ (2 pts.) for 12 hours at 180° (Balsohn, *Bl.* [2] 32, 617).—4. According to Berthelot (*Bl.* [2] 9, 289) it is among the products obtained by heating naphthalene with conc. HIAq (20 pts.).—5. According to Friedel a. Crafts (*Bl.* [2] 39, 195) it is among the carbonaceous products of the action of Al_2Cl_6 on benzene at 200°.—6. By heating styrene with HIAq (20 pts.) (Berthelot, *Bl.* [2] 9, 455).

Properties.—Liquid, resembling toluene.

Reactions.—1. On passing through a *red-hot tube* it is decomposed forming styrene (2 p.c.) benzene (15 p.c.), toluene (1 p.c.), naphthalene (2·2 p.c.), naphthalene dihydride, diphenyl (·6 p.c.), phenanthrene (2·6 p.c.), and anthracene (·4 p.c.) (Berthelot, *Z.* [2] 4, 589; Ferko, *B.* 20, 663). 2. By prolonged *oxidation* with dilute HNO_3 or CrO_3 it is converted into benzoic acid. When the oxidation is incomplete there is formed a small quantity (10 p.c.) of acetophenone (Friedel a. Balsohn, *Bl.* [2] 32, 615).—3. In carbon disulphide it yields with chromyl chloride CrO_2Cl_2 a chocolate crystalline pp. of composition $PhEt2CrO_2Cl_2$ converted by moisture into phenyl-acetic aldehyde (Étard, *A. Ch.* [5] 22, 246).—4. Converted by boiling with Al_2Cl_6 into *p*-di-ethyl-benzene and a little *m*-di-ethyl-benzene (Anschütz, *A.* 235, 189).—5. *Chlorine* under the influence of light forms α-chloro-ethyl-benzene (Schramm, *M.* 8, 101).—6. By the action of *bromine* in the dark, or of bromine in presence of 3 p.c. of iodine in diffused daylight it yields a mixture of *o*- and *p*-bromo-ethyl-benzene (Schramm, *B.* 18, 1272; *M.* 8, 304).

***m*-Di-ethyl-benzene.** [−20°]. (182°). S.G. $\frac{20}{4}$ ·8602. Formed, together with the *p*-isomeride, when benzene is acted upon by EtBr in presence of $AlCl_3$ (Voswinkel, *B.* 21, 2829). Forms no compound with picric acid. Dilute HNO_3 gives isophthalic acid. Gives $C_6H_3BrEt_2$ (238°) and $C_6Br_4Et_2$ [74°].

***p*-Di-ethyl-benzene** $C_{10}H_{14}$ *i.e.* $C_6H_4(C_2H_5)_2$. Mol. w. 134. (181°) (A.). S.G. $\frac{15·5}{}$ ·871.

Formation.—1. From *p*-di-bromo-benzene [89°] by treatment with sodium and EtI (Aschenbrandt, *A.* 216, 212; *B.* 12, 1303).—2. From *p*-bromo-ethyl-benzene, Na and EtI (Fittig, *A.* 144, 285).—3. A di-ethyl-benzene (179°–185°) is formed by passing ethylene into benzene containing Al_2Cl_6 (Balsohn, *Bl.* [2] 31, 540; Friedel a. Crafts, *A. Ch.* [6] 14, 456).—4. By passing EtCl into benzene containing Al_2Cl_6 a di-ethyl-benzene is formed which on oxidation by chromic mixture gives an acid $C_6H_4(CO_2H).CH_2CO_2H$ subliming at 210° (Allen a. Underwood, *Bl.* [2] 40, 100).

Reactions.—1. Gives ethyl-benzoic acid on *oxidation* by dilute HNO_3. Chromic acid mixture forms terephthalic acid.—2. CrO_2Cl_2 forms a compound $C_6H_4Et_22CrO_2Cl_2$ converted by water into phenyl-acetic aldehyde (Étard, *A. Ch.* [5] 22, 252).

***s*-Tri-ethyl-benzene** $C_{12}H_{18}$ *i.e.* $C_6H_3Et_3$ [1:3:5]. (218°). Formed by treating a mixture of acetone and methyl ethyl ketone with H_2SO_4 (Jacobsen, *B.* 7, 1430). It yields trimesic acid $C_6H_3(CO_2H)_3$ on oxidation. Tri-ethyl-benzenes are also formed by the action of ethylene on benzene in presence of Al_2Cl_6 (Friedel a. Crafts, *A. Ch.* [6] 14, 456), the chief product being *s*-tri-ethyl-benzene. On oxidation by CrO_3 this mixture gives an acid $C_{10}H_8O_6$ crystallising in large needles, and ultimately trimesic acid (Friedel a. Balsohn, *Bl.* [2] 34, 635).

s-Tetra-ethyl-benzene $C_6H_2Et_4$[1:2:4:5]. [13°]. (250°). Formed, together with the consecutive isomeride, by the action of EtBr and $AlCl_3$ on benzene; the product (250°–255°) is treated with $ClSO_3H$, and the sodium salts of the resulting sulphonic acids crystallised from water. The Na salt of *s*-tetra-ethyl-benzene sulphonic acid crystallises first, and the residual acid is converted into Ba salt. After barium *c*-tetra-ethylbenzene sulphonate has crystallised, there may still be obtained from the mother-liquor a sulphamide [100°], possibly belonging to *i*-tetra-ethyl-benzene. The sulphonic acids are hydrolysed (Jacobsen, *B.* 21, 2820). Crystalline mass; oxidised by dilute HNO_3 and by $KMnO_4$ to pyromellitic acid. Br gives $C_6Br_2Et_4$ [112·5°].

c-Tetra-ethyl-benzene $C_6H_2(C_2H_5)_4$[1:2:3:4]. (254° cor.). V.D. (H = 1) 189·5 (obs.). Colourless liquid. Lighter than water. Prepared by heating benzene with ethyl bromide and Al_2Cl_6 at 100°. On oxidation with $KMnO_4$ it gives prehnitic acid $C_6H_2(CO_2H)_4$ (Galle, *B.* 16, 1745). Forms $C_6Br_2Et_4$ [77°] (J.).

Penta-ethyl-benzene C_6HEt_5. (277°). S.G. $\frac{19}{19}$ ·8985. Obtained from benzene by the action of EtBr and $AlCl_3$. Purified by conversion into the sulphonic acid by $ClSO_3H$, crystallisation of the Na salt, and subsequent hydrolysis (Jacobsen, *B.* 19, 1209; 20, 896, 2857; 21, 2814). Oil. Does not solidify at −20°. HNO_3 does not give a nitro-compound. When treated with conc. H_2SO_4, followed by fuming H_2SO_4 there is formed $C_6H_2Et_4$ and C_6Et_6.

Hexa-ethyl-benzene $C_6(C_2H_5)_6$. [129°]. (298° cor.). V.D. (H = 1) 242·1 (obs.). Formed by heating benzene with ethyl bromide and Al_2Cl_6 at 100° (Galle, *B.* 16, 1745; Jacobsen, *B.* 21, 2820). Formed also by passing EtCl into benzene containing Al_2Cl_6 (Albright, Morgan, a. Woolworth, *C. R.* 86, 887). Long colourless monoclinic prisms. Sol. alcohol and ether, sl. sol. acetic acid. Easily sublimes.

References.—Bromo-, Bromo-nitro-, Chloro-, Chloro-nitro-, Nitro-, &c., ethyl-benzene.

ETHYL-BENZENE CARBOXYLIC ACID *v.* Phenyl-propionic acid.

Ethyl-benzene di-carboxylic acid $C_{10}H_{10}O_4$ *i.e.* $CO_2H.C_6H_4.CHMe.CO_2H$. [147°]. From its nitrile and fuming HCl at 200° (Gabriel, *B.* 20, 2504). Crystalline powder.

Nitrile $CN.C_6H_4.CHMe.CN$. [37°]. (285°). From $CN.C_6H_4.CH_2CN$ by treatment with alcoholic KOH and MeI. Triclinic prisms (Fock, *B.* 20, 2501). V. sol. alcohol and ether. Conc. H_2SO_4 at 125° converts it quickly into the imide $C_6H_4<\begin{matrix}\text{CHMe.CO}\\\text{CO---NH}\end{matrix}$ [145°], whence $POCl_3$ at 200° gives chloro-oxy-methyl-isoquinoline.

Isomeride *v.* Carboxy-phenyl-propionic acid.

ETHYL-BENZENE SULPHONIC ACID $C_6H_4Et(SO_3H)$. Two acids of this composition are obtained by digesting ethyl-benzene with fuming H_2SO_4 at 100°. The more abundant acid forms the less soluble K salt, which crystallises well and yields an amide [108°]; fused with KOH it yields solid ethyl-phenol (Chrustschoff, *B.* 7, 1166).

***m*-Ethyl-benzene sulphonic acid** $C_6H_3Et_2SO_3H$ [1:3:4 ?]. From the hydrocarbon and $ClSO_3H$ (Voswinkel, *B.* 21, 2830).—KA′aq: dimetric tables.—BaA′₂ 3aq: prisms, m. sol. water.—CuA′₂ 4aq: blue plates.

Amide $C_6H_3Et_2SO_2NH_2$: [102°]; needles (from alcohol).

***p*-Di-ethyl-benzene sulphonic acid** $C_6H_3Et_2(SO_3H)$. From di-ethyl-benzene and fuming H_2SO_4 (Fittig a. König, *A.* 144, 277; Aschenbrandt, *A.* 216, 214; Remsen a. Noyes, *Am.* 4, 200). Deliquescent laminæ.

Salts.—KA′ 3½aq.—NaA′.—BaA′₂ 4aq: leaflets. S. (of BaA′₂) 5·1 at 23°.—SrA′₂ 4aq.—CaA′₂ 5aq.—CuA′₂ 6aq: blue plates.—PbA′₂ 3aq.—HgA′₂.—NiA′₂ 5aq.—CoA′₂ 5aq.—MgA′₂.—AgA′.

Amide $C_6H_3Et_2(SO_2NH_2)$. [97·5° cor.] Leaflets, sl. sol. water.

***s*-Tetra-ethyl-benzene sulphonic acid** $C_6HEt_4SO_3H$. From *s*-tetra-ethyl-benzene and $ClSO_3H$ (Jacobsen, *B.* 21, 2820).—NaA′₂ 4aq: plates (from water), or tables (from alcohol); sl. sol. cold water, insol. dilute NaOHAq.—BaA′₂ 9aq: scaly crystalline pp. Sl. sol. boiling water.

Amide $C_6HEt_4SO_2NH_2$: [122°]; trimetric plates (from dilute alcohol).

***c*-Tetra-ethyl-benzene sulphonic acid** $C_6H(C_2H_5)_4SO_3H$. Silky plates or long needles. Formed by sulphonation of *c*-tetra-ethyl-benzene.

Salts.—A′Na 5aq: microscopic plates.—A′₂Ba 6aq: flat prisms.—A′₂Cu 8aq: light-blue plates.—A′₂Cd 7aq: large flat prisms.

Amide $C_6H(C_2H_5)_4SO_2NH_2$: [107°]; glistening scales or large monoclinic prisms, v. sol. alcohol and acetic acid, sl. sol. petroleum-ether (Galle, *B.* 16, 1745).

Penta-ethyl-benzene sulphonic acid $C_6Et_5SO_3H$. From penta-ethyl-benzene and $ClSO_3H$ (Jacobsen, *B.* 21, 2814).—NaA′ 4aq: thin pearly plates (from water); m. sol. cold water, insol. dilute NaOHAq, v. sol. alcohol.—KA′ 2aq: six-sided, trimetric plates (from water), prisms (from alcohol); sl. sol. cold, m. sol. hot, water, v. e. sol. alcohol.—NH_4A′ aq: trimetric, six-sided plates, sl. sol. cold water.—BaA′₂ 9aq: from the Na salt and $Ba(OAc)_2$. Small scales; v. sl. sol. boiling water.

Reference.—Chloro-ethyl-benzene sulphonic acid.

ETHYL-BENZHYDROXAMIC ETHER *v.* Benzenyl-ethoxim ethyl ether.

TETRA-ETHYL-BENZIDINE *v.* Tetra-ethyl-di-amido-diphenyl.

ETHYL BENZOATE *v.* *Ethyl ether* of Benzoic acid.

***o*-ETHYL-BENZOIC ACID** $C_9H_{10}O_2$ *i.e.* $C_6H_4EtCO_2H$[1:2]. Mol, w. 150. [68°]. Formed by reduction of tri-chloro-, or di-chloro-bromo-, vinyl-benzoic acid with sodium amalgam (Zincke, *B.* 20, 2056). Formed also by reduction of acetophenone carboxylic acid or of phthalyl-acetic acid $C_6H_4(C_2O_2)CH.CO_2H$ with HI and P at 180° (Gabriel a. Michael, *B.* 10, 2206).—Slender flat needles.—AgA′: long needles.

***m*-Ethyl-benzoic acid** $C_6H_4Et.CO_2H$ [1:3]. [47°]. Formed by oxidising *m*-di-ethyl-benzene with dilute HNO_3 (Jacobsen, *B.* 21, 2820). Needles, insol. cold water.—CaA′₂ 4aq: needles, v. sol. water.

***p*-Ethyl-benzoic acid** $C_6H_4Et.CO_2H$[1:4]. [113°].

Formation.—1. By the action of sodium and CO_2 upon *p*-bromo-ethyl-benzene (Kekulé, *A.*

137, 178; Kekulé a. Thorpe, *C. J.* 22, 366).—2. By oxidising di-ethyl-benzene with boiling dilute HNO_3 (Fittig a. König, *A.* 144, 277; Aschenbrandt, *A.* 216, 218).

Properties.—Small plates (from water) or prisms (from alcohol), v. sl. sol. cold water, v. sol. alcohol, ether, chloroform, and benzene. May be sublimed. Melts under water. Gives terephthalic acid on oxidation.

Salts.—BaA'_2 2aq (A.).—BaA'_2 aq (F. a. K.). S. 2.—CaA'_2 3aq (A.)—CaA'_2 2aq (F. a. K.): feathery tufts of needles.—CuA'_2 *x*aq.—AgA': needles (from hot water).

Di-ethyl-benzoic acid $C_{11}H_{14}O_2$ *i.e.* $C_6H_3Et_2.CO_2H$. Formed, together with benzoic acid, by fusing di-ethyl-carbobenzoic acid $C_{18}H_{18}O_2$ with potash (Zagoumenny, *A.* 184, 171). Oil.—AgA': laminæ (from water).

References.—Chloro- and Nitro- ethyl-benzoic acids.

ETHYL-BENZOPHENONE *v.* Phenyl-ethyl-phenyl-ketone.

ETHYL-BENZOYL-ACETIC ACID *v.* Benzoyl-acetic acid.

ETHYL-BENZYL- *v.* Benzyl-ethyl-.

ETHYL-DIBENZYL *v.* Phenyl-ethyl-phenyl-ethane.

ETHYL-DI-BENZYL-PHOSPHINE $EtP(C_7H_7)_2$. (320°–330°). Formed by treating with NaOH the distillate from $Et_2P(C_7H_7)_2Cl$ (*v. infra*) (Collie, *C. J.* 53, 725).

Benzylo-chloride $EtP(C_7H_7)_3Cl$ aq. Decomposed on distillation, giving ethylene, stilbene, HCl, &c.

Di-ethyl-benzyl-phosphine $Et_2PC_7H_7$. (250°–255°). Formed by distilling $Et_3PC_7H_7Cl$ and treating the resulting $Et_2PC_7H_7ClH$ with NaOH (Collie, *C. J.* 53, 724).

Oxide $Et_2(C_7H_7)PO$. (329°). Formed as above, and also by heating $Et_2(C_7H_7)_2POH$. Long needles. Converted by Na into $Et_2PC_7H_7$.

Sulphide $Et_2(C_7H_7)PS$. [95°]. (300°–310°). Formed by adding S to an ethereal solution of $Et_2PC_7H_7$. Crystalline; insol. water. When heated with Na the phosphine $Et_2PC_7H_7$ is liberated.

Benzylo-chloride $Et_2P(C_7H_7)_2Cl$. Decomposed on heating into C_2H_4 and $EtP(C_7H_7)_2ClH$.

ETHYL BENZYL SULPHIDE *v. Ethyl derivative* of Benzyl mercaptan.

TRI-ETHYL-BISMUTHINE *v.* Bismuth tri-ethide.

TRI-ETHYL-BIURET $C_8H_{17}N_3O_2$ *i.e.* $NEt(CO.NHEt)_2$. Formed by warming cyanuric ether with baryta (Limpricht a. Habich, *A.* 109, 104; Nencki, *B.* 9, 1011). Thick oil, sl. sol. water, v. sol. alcohol and ether. Split up on distillation into cyanic ether and di-ethyl-urea.

ETHYL BORATES.

Ethyl ortho-borate $(C_2H_5)_3BO_3$. (120° i.V.). S.G.$_0$ ·887; $^{26·5}$ ·861. V.D. 5·14 (calc. 5·07). Prepared by the action of alcohol on BCl_3 (Ebelmen a. Bouquet, *A. Ch.* [3] 17, 55; Bowman, *P. M.* [3] 29, 546). Formed also by distilling a mixture of dry $KEtSO_4$ with anhydrous borax (Rose, *P.* 98, 245), and by the action of absolute alcohol as powdered B_2O_3 (Schiff, *Bl.* [2] 5, 372; 6, 36). Colourless liquid with alcoholic odour. Burns with green flame. Mixes with ether and alcohol. Decomposed by water in a few minutes into alcohol and boric acid. HNO_3 gives nitric ether and boric acid. Acetic acid forms acetic ether and B_2O_3. PCl_5 forms EtCl, $POCl_3$ and $EtBO_2$.

Ethyl metaborate $EtBO_2$. Among the products of the action of alcohol on B_2O_3. Dense liquid, absorbs moisture from the air, being split up into alcohol and boric acid. Gives with alcohol Et_3BO_3. Acetic acid at 190° gives acetic ether and HBO_2. Cannot be distilled, for it splits up at high temperatures into Et_3BO_3 and gummy EtB_3O_5, which behaves like $EtBO_2$ towards water and alcohol.

ETHYL-BORIC ETHER $EtB(OEt)_2$. The compound $EtB(OEt)_2,B(OEt)_3$ (112°) is formed by action of $ZnEt_2$ (2 mols.) on boric ether (1 mol.). Water decomposes it into ethyl-boric acid $BEt(OH)_2$ and alcohol (Frankland, *Pr.* 25, 165).

Di-ethyl-boric ether $Et_2B.OEt$ (103°). From $ZnEt_2$ and $EtB(OEt)_2,B(OEt)_3$. Dry oxygen converts it into $BEt(OEt)_2$. Water converts it into diethyl-boric acid $Et_2B.OH$, which absorbs oxygen from air, forming crystals of EtB(OEt).OH, whence H_2O forms alcohol and $EtB(OH)_2$.

ETHYL BROMIDE C_2H_5Br. *Bromo-ethane.* Mol. w. 109. (38·4°). S.G. $\frac{15}{4}$ 1·4189 (Mendelejeff); 1·4555 (Weegman, *Z. P. C.* 2, 218); $\frac{15}{15}$ 1·4499; $\frac{25}{25}$ 1·4325. M.M. 5·851 at 19·7°. S.V. 77·07 (Schiff). *Critical temperature*: 236° (Pawlewsky, *B.* 16, 2633).

Formation.—1. The rate of formation from alcohol and HBr has been studied by Villiers (*C. R.* 90, 1488).—2. When a mixture of ethylene and HBr is passed over Al_2Br_6 there is formed $Al.Br_3C_4H_8$, ethyl bromide, and saturated hydrocarbons (Gustavson, *J. pr.* [2] 34, 161).—3. Together with other products by heating alcohol (1 pt.) with bromine (3 pts.) (Lowig, *A.* 3, 291).

Preparation.—1. By adding bromine (8 pts.) gradually to alcohol (40 pts.), mixed with clear phosphorus (1 pt.), and distilling (Serullas, *A. Ch.* 34, 99). Personne (*C. R.* 52, 468) employed red phosphorus (40 g.) with dry alcohol (160 g.) and bromine (100 g.).—2. By mixing H_2SO_4 (10 pts.) and alcohol (5 pts.), allowing to stand for some time, and then diluting with water (3 pts.), adding KBr (5 pts.) and distilling. The yield is 80 to 100 p.c. (De Vrij, *J. Ph.* [3] 31 169; *cf. C. J.* 36, 127; *D. P. J.* 229, 284).

Properties.—Colourless liquid with ethereal odour and anæsthetic influence (Robin, *C. R.* 32, 649). V. sl. sol. water, miscible with alcohol and ether. Burns with difficulty, forming a smokeless green flame. Not acted upon by HNO_3, by H_2SO_4, or by potassium.

Reactions.—1. When passed through a *red-hot tube* ethylene and HBr are among the products.—2. *Ammonia* gives èthylamines. Other bases act similarly.—3. *Alcoholic potash* forms KBr and ether (Berthelot, *A.* 92, 351).—4. *Bromine* forms $CH_3.CHBr_2$, $CH_2Br.CH_2Br$, and $CH_2Br.CHBr_2$ (114°) (Tavildaroff, *A.* 176, 12).—5. The dry *copper-zinc couple* forms BrZnEt, the combination being facilitated by the presence of a little EtI. In presence of water or alcohol ethane is given off on warming (Gladstone a. Tribe, *C. J.* 27, 410).—6. A mixture of EtBr passed over Al_2Br_6, or the compound $AlBr_3C_4H_8$ at 60° gives saturated hydrocarbons (Gustavson).

Compound $EtBrH_2S$ 23aq (Forcrand, *A. Ch.* [5] 28, 29).

ETHYL-BROMO-ACETO-ACETIC ETHER *v.* Bromo-aceto-acetic ether.

ETHYL-DI-BROMO-DI-ALLYL-AMINE $C_8H_{13}Br_2N$ *i.e.* $EtN(C_3H_4Br)_2$. From dibromo-allyl-amine and EtI at 100° (Maxwell Simpson, *P. M.* [4] 16, 257). Pungent bitter oil, alkaline to test papers. Precipitates $Cu(OH)_2$ from cupric salts.

ETHYL BROMO-ALLYL OXIDE C_5H_9BrO *i.e.* $Et.O.CH_2.CBr{:}CH_2$. (133°). S.G. $\underline{12}$ 1·26. From $EtO.CH_2.CHBr.CH_2Br$ and NaOH (Henry, *B.* 5, 188).

Ethyl di-bromo-allyl oxide $Et.O.CH_2.CBr{:}CHBr$. From ethyl propargyl oxide and Br (Liebermann a. Kretschmer, *A.* 158, 234).

ETHYL-BROMO-AMINE *v.* Ethylamine.

ETHYL-BROMO-ANILINE *v.* Bromo-ethyl-aniline.

ETHYL BROMO-PENTENYL OXIDE $C_5H_8Br.O.Et$. (179°). S.G. $\underline{12}$ 1·23. From bromo-amylene bromide(tri-bromo-pentane) and alcoholic KOH (Reboul, *A.* 133, 84).

ETHYL-BROMO-PODOCARPIC ACID *v.* Podocarpic acid.

ETHYL ISOBUTYL CARBONATE $C_7H_{14}O_3$ *i.e.* $Et(C_4H_9)CO_3$. (160·1° cor.). S.G. $\underline{27}$ ·92 (Röse, *A.* 205, 230).

ETHYL-ISOBUTYL-GLYOXALINE $C_9H_{16}N_2$ *i.e.* $C_3H_2Et(C_4H_9)N_2$. *Oxalethylisoamyline.* (225°). S.G. $\underline{19{\cdot}6}$ ·9291. The hydrobromide is formed from isobutyl-glyoxaline (glyoxal-isoamyline) and EtBr (Radziszewsky a. Szul, *B.* 17, 1294). Oil.—$B'_2H_2PtCl_6$: orange prisms.

ETHYL ISOBUTYL KETONE $C_2H_5.CO.CH_2Pr$. (135°) at 735 mm. S.G. $\frac{0}{0}$ ·829; $\frac{15}{0}$ ·815. Formed when CO is passed over a mixture of sodium isovalerate and NaOEt at 160° (Loos, *A.* 202, 327). Also from isovaleryl chloride and $ZnEt_2$ (Wagner, *Bl.* [2] 38, 264; *J. R.* 16, 673). Gives on oxidation acetic and isovaleric acids.

Ethyl *tert*-**butyl ketone** $Et.CO.CMe_3$. (126°). S.G. ^{0} ·831; $\underline{12}$ ·810. From $CMe_3.COCl$ and $ZnEt_2$ (Wyschnegradsky, *A.* 178, 104). Liquid smelling of mint and camphor. Oxidised by CrO_3 to CMe_3CO_2H.

ETHYL-BUTYL-OXIDE $C_6H_{14}O$ *i.e.* $Et.O.C_4H_9$. (91·4°). S.G. $\frac{0}{0}$ ·768. S.V. 150·1. C.E. (0°–10°) ·00116 (Dobriner, *A.* 243, 5; *cf.* Lieben a. Rossi, *A.* 158, 167).

Ethyl isobutyl oxide $EtOCH_2Pr$. (79°). S.G. ·75. From EtI and KOC_4H_9 (Wurtz, *A. Ch.* [3] 42, 129; *A.* 93, 117) or from C_4H_9Br and KOEt (Meissler, *C. C.* 1887, 479).

Ethyl tert-butyl oxide $EtOCMe_3$. (69°). Formed by heating tert-butyl bromide (2 vols.) with NEt_3 (5 vols.) and alcohol (5 vols.) at 100° (Reboul, *J.* 1881, 409).

ETHYL ISOBUTYL SULPHATE? $Et(C_4H_9)SO_4$. From $C_4H_9O.SO_2Cl$ and alcohol (Behrend, *J. pr.* [2] 15, 34). Decomposed by water into alcohol and $H(C_4H_9)SO_4$.

ETHYL ISOBUTYL (α)-THIOCARBONATE $EtO.CO.SC_4H_9$. (192°). S.G. $\underline{10}$ ·994. From $ClCO_2Et$ and $NaSC_4H_9$ (Mylius, *B.* 6, 313).

Ethyl-isobutyl (α)-di-thio-carbonate $EtS.CO.OC_4H_9$. (193°). S.G. $\underline{10}$ ·994. From $ClCO_2C_4H_9$ and NaSEt (M.); *v.* Ethyl thiocarbonates.

Ethyl-isobutyl dithiocarbonate $C_4H_9O.CS.SEt$. (228°). From $C_4H_9O.CS.SK$ and EtI at 100° (Mylius, *B.* 5, 972). Yellow liquid with unpleasant odour, with a taste like aniseed.

ETHYL CAMPHENE $C_{10}H_{15}(C_2H_5)$. (198°–200° cor.) at 742 mm. S.G. $\underline{20}$ ·9709. V.D. = 5·55 (found). Prepared by the action of sodium on a mixture of solid camphor-dichloride [155°] and ethyl iodide (Spitzer, *B.* 11, 1817). Mobile fluid of turpentine-like smell.

ETHYL-CAMPHOR *v.* Camphor.

ETHYL CARBAMATE *v.* vol. i. p. 679.

ETHYL - CARBAMIC ACID $NHEt.CO_2H$. Ethyl-ammonium salt NH_3EtA'. From ethylamine and CO_2 at −18°. Snow-white powder. Decomposed by water although, like ammonium carbamate, it does not immediately ppt. $BaCl_2$ in the cold (Wurtz, *A. Ch.* [3] 30, 443).

Ethyl ether $NEtH.CO_2Et$. (176°). V.D. 4·07. S.G. $\underline{21}$ ·986. From $ClCO_2Et$ and $NEtH_2$ (Schreiner, *J. pr.* [2] 21, 125; 22, 353). Formed also by heating cyanic ether with alcohol in sealed tubes at 100° (Wurtz, *C. R.* 37, 182). Oil. Decomposed by potash into ethylamine, alcohol, and K_2CO_3.

Di - ethyl - carbamic chloride $Cl.CO.NEt_2$. *Chloro-formic acid diethylamide.* (190°–195°). Prepared by the action of PCl_5 on diethyl-oxamic acid, CO being evolved (Wallach, *B.* 14, 746). Liquid. By treatment with diethylamine it gives tetra-ethyl-urea. By water it is decomposed into CO_2 and diethylamine hydrochloride.

ETHYL CARBAMINE CNC_2H_5. (78°). Mol. w. 55. From ethyl iodide and silver cyanide (*v.* vol. i. p. 680). Also from EtI and mercuric fulminate (Calmels, *J. pr.* [2] 30, 319). Stinking liquid. Does not solidify at −68°. Split up by acids into formic acid and ethylamine. HgO added to a solution of ethyl carbamine (1 vol.) in ether (4 vols.) forms $C_9H_{22}N_4O_2$ [112°]. Br forms oily $NC_3H_5Br_2$ (Tscherniak, *Bl.* [2] 30, 105).

Ethyl - carbamine cyamide *v.* Carbimido-ethyl-urea.

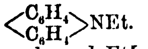
DI-ETHYL SEMI-CARBAZIDE $C_3H_9N_3O$ *i.e.* $NH_2.CO.N_2H_2Et$. [106°]. From ethyl-hydrazine hydrochloride and conc. aqueous potassium cyanate (Fischer, *A.* 199, 284). Laminæ; v. e. sol. water and alcohol, sl. sol. ether and conc. alkalis. Reduces Fehling's solution and HgO only when warm.

s - Di - ethyl - semicarbazide $C_5H_{13}N_3O$ *i.e.* $NHEt.CO.NEt.NH_2$. From the nitrosamine of s-di-ethyl-urea NHEt.CO.NEt.NO by reduction with zinc-dust and HOAc in alcoholic solution (Fischer, *A.* 199, 284). Crystallises with difficulty; v. sol. water and alcohol. Reduces Fehling's solution only when warm. Boiling conc. HClAq splits it up into CO_2, ethyl-hydrazine, and NH_2Et.—B'HCl: slender needles.—$B'_2H_2PtCl_6$.

***u*-Di-ethyl-semi-carbazide** $NH_2.CO.NH.NHEt$. [149°]. Formed by the action of potassium cyanate on the neutral salts of *u*-di-ethyl-hydrazine (F.). Long slender prisms (from alcohol); v. e. sol. alcohol and hot water, v. sl. sol. ether. Reduces boiling Fehling's solution with much difficulty. — $B'_2H_2PtCl_6$: slender yellow needles (from alcohol).

Nitrosamine $NH_2CO.N(NO).NEt_2$. Yellow plates; sl. sol. water, v. sol. alcohol and ether. Dilute KOH splits it up at once into diethylamine, CO_2, ammonia, and N_2O.

ETHYL-CARBAZOLE $C_{14}H_{13}N$ *i.e.*



$<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>NEt$. [67°]. From potassium carbazole and EtI (Graebe, *A.* 202, 23). Leaflets, sol. ether and hot alcohol insol. water. Its picrate $C_{14}H_{13}NC_6H_2(NO_2)_3OH$ crystallises in needles [97°].

ETHYL-CARBAZOLINE $C_{14}H_{19}N$ *i.e.* $C_{12}H_{14}NEt$. Hydroiodide B'HI. From carbazoline, EtI, and alcohol at 100° (Graebe a. Behaghel, *A.* 202, 25). Thick tables, v. sol. hot water.

ETHYL - CARBIMIDO - METHYL - THIO - UREA

$SC<\begin{matrix}NMe\\NH\end{matrix}>C:NEt$ or MeNH.CS.N:C:NEt. *Methyl-thio-carbamine-ethyl-cyamide.* [106°]. Formed by the action of ethyl iodide upon sodium carbimido-methyl-thiourea (Wunderlich, *B.* 19, 448).

ETHYL-CARBIMIDO-PHENYL-THIO-UREA

$SC<\begin{matrix}NPh\\NH\end{matrix}>C:NEt$ or PhNH.CS.N:C.NEt. *Phenyl-thio-carbamine-ethyl-cyamide.* [119°]. Formed by the action of ethyl-iodide upon sodium carbimido-phenyl-thio-urea. Crystalline solid. V. sol. water and alcohol. Indifferent body (Wunderlich, *B.* 19, 448).

ETHYL-CARBIMIDO-UREA

$OC<\begin{matrix}NH\\NH\end{matrix}>C:NEt$ or $H_2N.CO.N:C:NEt$. *Carbamine-ethyl-cyamide.* [121°]. Formed by the action of ethyl iodide upon sodium carbimido-urea ('amido-dicyanic acid'). Neutral body (Wunderlich, *B.* 19, 448).

DI-ETHYL-CARBINOL *v.* AMYL ALCOHOL.

Tri-ethyl-carbinol *v.* HEPTYL ALCOHOL.

DI-ETHYL-CARBINYL *v.* AMYL.

DI-ETHYL-CARBOBENZOIC ACID $C_{18}H_{18}O_2$ or $C_{16}H_{16}O_2$? [102°]. (239°) at 11 mm. An acid formed when deoxybenzoin is heated with alcoholic KOH (Limpricht a. Schwanert, *A.* 155, 66; Zagoumenny, *A.* 184, 163; Anschutz a. Berns, *B.* 20, 1392). Slender needles (from ether). Converted by potash-fusion into benzoic and di-ethyl-benzoic acids. Dilute H_2SO_4 forms crystalline $C_{18}H_{18}O_2$ [132°] and other bodies. HNO_3 gives a di-nitro-derivative [156°].

Salts. AgA': amorphous.—EtA': oil.

ETHYL CARBONATE $C_5H_{10}O_3$ *i.e.* Et_2CO_3. Mol. w. 118½. (126° cor.) (Kopp, *A.* 95, 325). S.G. $\frac{20}{4}$ ·9762. $\mu_\beta = 1·3897$. R_∞ - 45·41 (Bruhl, *A.* 203, 23). H F.p. 152,500. H.F.v. 149,310 (*Th.* 4, 213). H.C. 641,148 (Louguinine, *Bl.* [2] 41, 389). V.D. 4·09 (obs. and calc. Cahours).

Formation.—1. By the action of potassium or sodium on oxalic ether at 130°, the metal being added as long as CO escapes; water is then added, and the Et_2CO_3 dried over $CaCl_2$ and rectified (Ettling, *A.* 19, 17).—2. By distilling a mixture of $KEtCO_3$ with $KEtSO_4$ (Chancel, *C. R.* 31, 521).—3. By the action of NaOEt on oxalic ether (Cranston a. Dittmar, *C. J.* 22, 441).—4. From $ClCO_2Et$ and NaOEt (Schreiner, *J. pr.* [2] 22, 353).

Properties.—Colourless liquid, burning with blue flame. Insol. water, v. sol. alcohol and ether. Chlorine gives products of substitution (Cahours, *A. Ch.* [3] 9, 201). Saturated with HBr and heated to 100° there are formed EtBr, CO_2, and water (Gal, *C. R.* 59, 1049). By heating with sodium or NaOEt in sealed tubes it yields $NaEtCO_3$, carbonic oxide, and Et_2O (Geuther, *Z.* [2] 4, 656). Ammonia at 100° forms carbamic ether; at 180° ammonia gives urea (Natanson, *A.* 98, 287). PCl_5 gives EtCl and $ClCO_2Et$ (Geuther, *A.* 205, 247).

Potassium ethyl carbonate $KEtCO_3$. When CO_2 is passed into a solution of KOH in absolute alcohol there is formed a crystalline deposit consisting of $KEtCO_3$, $KHCO_3$, and K_2CO_3; the mass is washed with ether, the $KEtCO_3$ is then dissolved in alcohol and ppd. by ether (Dumas a. Peligot, *A. Ch.* [2] 74, 6). White nacreous salt; split up by water into alcohol and $KHCO_3$. $NaEtCO_3$ and amorphous $Ba(EtCO_3)_2$ are obtained by passing CO_2 into alcoholic solutions of NaOEt and $Ba(OEt)_2$ respectively (Beilstein, *A.* 112, 124; Destrem, *A. Ch.* [5] 27, 10).

Ethyl ortho-carbonate $C(OEt)_4$. Mol. w. 192. (159°). V.D. 6·80 (calc. 6·65). Sodium (24 g.) is added in small portions to a boiling solution of chloropicrin (40 g.) in absolute alcohol (300 g.); as soon as the reaction is finished the excess of alcohol is distilled off and water is added to the residue; the oil is then dried by $CaCl_2$ and rectified (Bassett, *C. J.* 17, 198). Oil, with peculiar aromatic odour. Decomposed by boiling alcoholic KOH. B_2O_3 at 100° forms boric ether and Et_2CO_3. Bromine forms EtBr, Et_2CO_3, bromal, &c. (Ladenburg a. Wichelhaus, *A.* 152, 166). Ammonia forms guanidine.

Reference: TETRA-CHLORO-DI-ETHYL CARBONATE.

ETHYL-CARBOPYRROL-AMIDE *v.* ETHYL-PYRROLE CARBOXYLIC ACID.

ETHYL-CARBOSTYRIL *v.* *Ethyl ether of* OXY-QUINOLINE and OXY-ETHYL-QUINOLINE.

ETHYL CARBYLAMINE *v.* ETHYL-CARBAMINE.

ETHYL CETYL OXIDE $(C_2H_5)(C_{16}H_{33})O$. [20°]. Fine white needles. From cetyl iodide and EtONa (Becker, *A.* 102, 220; Walder, *B.* 20, 1751).

ETHYL PERCHLORATE $C_2H_5ClO_4$. Obtained by distilling a mixture of $Ba(EtSO_4)_2$ with $Ba(ClO_4)_2$ in quantities of 4 g. at a time (to avoid explosion) (Clark, Hare, a. Boyle, *P. M.* [3] 19, 370; Roscoe, *C. J.* 15, 213). The distillate separates into two layers, the upper one consisting of water which may be removed by blotting-paper. Colourless heavy oil, with pleasant odour and sweet taste. Explodes on the least provocation with excessive violence. It may be kept under water or in alcoholic solution. It may be distilled under a layer of water, passing over at 74°. It is immediately saponified by alcoholic potash.

ETHYL CHLORIDE C_2H_5Cl. *Chloro-ethane.* Mol. w. 64½. (12·5°) (Regnault, *J.* 1863, 67). S.G. $\frac{0}{0}$ ·9230; $\frac{6}{6}$ ·9171 (Perkin, *C. J.* 45, 449). V.D. 2·22 (calc. 2·24). H.F.p. (gaseous) 28,000; (liquid) 34,400 (Berthelot); 30,710 (Thomsen, *Th.*). H.F.v. 29,550 (*Th.*). M.M. 4·039 at 5° (P.). S.V. 75·8 (Ramsay).

Formation. — 1. By chlorinating ethane (Schorlemmer, *C. R.* 58, 703; *A.* 132, 234).—2. By the action of HCl on alcohol alone or in presence of $ZnCl_2$ (Robiquet a. Colin, *A. Ch.* [2]

1, 843; Regnault, *A. Ch.* [2] 71, 355; Kuhlmann, *A.* 33, 108; Löwig, *P.* 45, 346).—3. By the action of SCl, PCl_5, Al_2Cl_6, $SbCl_5$, Fe_2Cl_6, $SnCl_4$, &c., on alcohol.—4. From EtI and chlorine.—5. By treating acetic and other ethers with HCl.

Preparation.—1. HCl is passed into a boiling solution of $ZnCl_2$ (2 pts.) in 95 p.c. alcohol (3 pts.) in a flask with inverted condenser. The escaping gas is washed with water. The yield is nearly the theoretical (Groves, *C. J.* 27, 637).—2. By distilling a mixture of alcohol (5 pts.), H_2SO_4 (2 pts.), and NaCl (12 pts.).

Properties.—Gas, burning with green-edged flame. V. sl. sol. water, v. e. sol. alcohol and ether. Gives no pp. with silver nitrate solution in the cold.

Reactions.—1. Aqueous HI (S.G. 1·9) at 130° converts it into EtI.—2. SO_3 forms $ClSO_2.OEt$ (R. Williamson, *C. J.* 10, 100). By-products are also formed (Von Purgold, *B.* 6, 502).—3. Aqueous $AgNO_3$ at 100° gives a pp. of AgCl (G. C. Foster).—4. Boiling aqueous KOH slowly forms alcohol; alcoholic potash acts more readily, forming KCl, alcohol, and ether (Balard, *A. Ch.* [3] 12, 302).—5. *Ammonia* forms ethylamines (Groves, *C. J.* 13, 331). Equal volumes of C_2H_5Cl and NH_3 gas submitted to a pressure of 70 atmospheres for 48 hours at 175° do not react. The introduction of a small quantity of alcohol does not affect the result. In the cold an alcoholic solution of NH_3 and C_2H_5Cl requires to be kept several days before any action commences, and the reaction is not complete after several months (Vincent a. Chappuis, *Bl.* [2] 45, 503).—6. Alcoholic K_2S and KHS give Et_2S and mercaptan respectively (Regnault).—7. Passed over red-hot lime it forms acetic acid, CH_4, and hydrogen (L. Meyer, *A.* 139, 282; *cf.* Dumas a. Stas, *A. Ch.* [2] 73, 154).

Derivatives.—CHLORO-ETHANES and CHLORO-BROMO-ETHANES, ETHYLENE CHLORIDE and ETHYLIDENE CHLORIDE.

ETHYL-CHLORO-ACETO-ACETIC ETHER *v.* CHLORO-ACETO-ACETIC ETHER.

ETHYL CHLORO-ACETYLENE CARBOXYLIC ACID *v.* CHLORO-BUTANE CARBOXYLIC ACID.

ETHYL-DI-CHLORO-DI-ALLYL-AMINE $NEt(C_3H_4Cl)_2$. (c. 200). From $NH(C_3H_4Cl)_2$ and EtI at 100° (Engler, *Bl.* [2] 9, 134; *A.* 142, 81). Oil.—$B'_2H_2PtCl_6$: crystalline.

Di-ethyl-chloro-allyl-amine. *Ethylo-chloride* $C_3H_4Cl.NEt_3Cl$. Two compounds of this constitution are formed by heating *s*-tri-chloro-ethane $CH_2Cl.CHCl.CH_2Cl$ with NEt_3 (Reboul, *C. R.* 95, 993). They differ in the solubility of their Pt salts. Two di-chloro-propylenes appear to be intermediate in the formation of these ethylo-chlorides.

ETHYL α-CHLORO-ALLYL OXIDE C_5H_9ClO *i.e.* $Et.O.CH_2.CCl:CH_2$. (110°). S.G. $^{\underline{0}}$ 1·011; $^{\underline{21\cdot5}}$ ·995. From $CH_2:CCl.CH_2Cl$ and alcoholic KOH (Friedel a. Silva, *J.* 1872, 323). Formed also from ethyl allyl oxide by successive treatment with Cl and KOH (Henry, *B.* 5, 189).

Ethyl β-chloro-allyl oxide $Et.O.CH_2.CH:CHCl$. (120°–125°). S.G. $^{\underline{0}}$ 1·021; $^{\underline{25}}$ ·994. From $CH_2Cl.CH:CHCl$ and alcoholic KOH (F. a. S.). Br forms $EtO.CH_2.CHBr.CHClBr$ (220°).

ETHYL-CHLORO-AMINE *v.* ETHYLAMINE.

DI-ETHYL CHLORO-AMYL PHOSPHATE $Et_2(C_4H_9.CHCl)PO_4$. From $C_4H_9.CH_2.PO(OH)_2$ by successive treatment with PCl_5 and alcohol (Fossek, *M.* 7, 20).

ETHYL-CHLORO-ANILINE *v.* CHLORO-ETHYL-ANILINE.

TRI-ETHYL-CHLORO-AUROPHOSPHITE $Et_3PAuClO_3$. [c. –10°]. S.G. 2·025. Obtained by adding absolute alcohol to a mixture of AuCl and dry phosphorus and ppg. by water (Lindet, *C. R.* 103, 1014). Crystalline mass; decomposes about 100°. Insol. water, sol. alcohol, ether, and benzene. NH_3 forms $Et_3PAuClO_3N_2H_6$.

ETHYL-CHLORO-BENZENE *v.* CHLORO-ETHYL-BENZENE.

ETHYL-CHLORO-BROMO-PROPYL OXIDE $Et.CO.C_3H_5ClBr$. (187°). From epichlorhydrin and EtBr at 200° (Reboul a. Lourenço, *A.* 119 238).

ETHYL CHLORO-BUTENYL OXIDE $C_4H_6Cl.OEt$. (134°). From $CH_3.CH:CH.CHCl_2$ and alcoholic KOH (Kekulé, *A.* 162, 98).

ETHYL CHLORO-BUTYL OXIDE $CH_2Cl.CHEtOEt$. (141°). S.G. $^{\underline{0}}$ ·974. V.D. 69·3 (calc. 68·3). From $ZnEt_2$ and an ethereal solution of di-chloro-di-ethyl oxide (Lieben, *A.* 123, 130; 133, 287; 146, 220). Oil, miscible with alcohol and ether.

Reactions.—1. HI gives EtI and secondary butyl iodide.—2. With NaOEt it gives butylene glycol diethylic ether: $CH_2(OEt)CHEt.OEt$, (147°).—3. PBr_3 gives $CH_2Cl.CHEtBr$, ethyl bromide, and $CH_2Br.CHEtBr$.

ETHYL-CHLORO-ETHANE TETRA-CARBOXYLIC ACID *v.* CHLORO-BUTANE TETRA-CARBOXYLIC ACID.

ETHYL-CHLORO-MALONIC ETHER *v.* CHLORO-ETHYL-MALONIC ETHER.

ETHYL-DI-CHLORO-PHOSPHINE *v.* ETHYL-PHOSPHINE.

ETHYL CHLORO-ISOPROPYL OXIDE $CH_2Cl.CH.Me.OEt$. (118°). S.G. $^{\underline{0}}$ ·984. From $ZnMe_2$ and dichloro-diethyl ether (Lieben, *A.* 146, 225). PBr_3 gives MeBr, $CH_2Cl.CHMeBr$, and $CH_2Br.CHMeBr$.

ETHYL-CHLORO-QUINOLINE *v.* CHLORO-ETHYL-QUINOLINE.

ETHYL-CHLORO-SULPHATE *v.* ETHYL SULPHATE.

ETHYL CHRYSOÏDIN *v.* *Benzene*-Azo-*ethyl-phenylene-diamine.*

ETHYL-CINCHENIC ACID *v.* CINCHENE.

ETHYL-CINCHONAMINE *v.* CINCHONA BASES.

ETHYL-CINCHONIC ACID *v.* ETHYL QUINOLINE CARBOXYLIC ACID.

ETHYL-CINCHONIDINE *v.* CINCHONIDINE.

ETHYL-CINCHONINE *v.* CINCHONINE.

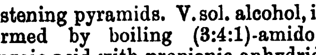
ETHYL-CITRIC ACID *v.* CITRIC ACID.

ETHYL-CODEÏNE *v.* CODEÏNE.

ETHYL-CONHYDRINE *v.* CONIÏNE.

ETHYL-CONIÏNE *v.* CONIÏNE.

ETHYL-COUMAZONIC ACID $C_{13}H_{15}NO_3$ *i.e.*



$$C_6H_3(CO_2H)\left\langle\begin{array}{l}CMe_2.O\\ \qquad\;|\\ N=CEt\end{array}\right.$$

(?). [202°]. Small glistening pyramids. V. sol. alcohol, insol. water. Formed by boiling (3:4:1)-amido-oxypropyl-benzoic acid with propionic anhydride.

Salts.—$A'H,HCl$: very soluble white needles.—$A'H,H_2SO_4$: very soluble white needles (Widmann, *B.* 16, 2576).

ETHYL CRESYL ETHER *v. Ethyl derivative of* CRESOL.

ETHYL-CROTONIC ACID *v.* HEXENOIC ACID.

ETHYL ISOCROTYL ETHER *v. Ethyl ether* of BUTENYL ALCOHOL, vol. i. p. 639.

ETHYL-CUMENE *v.* ETHYL-PROPYL-BENZENE.

ETHYL-CUMIDINE $C_{11}H_{17}N$ *i.e.* $C_6H_2Me_3NHEt$. (220°–230°). Formed by heating cumidine hydrochloride (1 mol.) with alcohol (1 mol.) for 4 hours at 125° (Ruttan, *B.* 19, 2383).

ETHYL CYANAMIDE *v. Cyanamide* under CYANIC ACID.

ETHYL-CYANIC ACID *v.* CYANIC ACID.

ETHYL CYANIDE *v.* PROPIONITRILE and ETHYL CARBAMINE.

ETHYL-CYANURIC ACID *v. Cyanuric acid* under CYANIC ACID.

ETHYLENE C_2H_4 *i.e.* $CH_2{:}CH_2$. Mol. w. 28. [−169°] (Olszewski, *M.* 8, 71); (−103°) (Cailletet, *C.R.* 94, 1224; Wroblewsky, *M.* 4, 338). V.D. ·9784 (Saussure; calc. ·9702). H.F.p. −8,000 (Favre a. Silbermann); −9,400 (Berthelot, *A. Ch.* [5] 23, 180); −4,160 (Thomsen, *J. pr.* [2] 23, 158); −2,710 (Thomsen, *Th.*). H.F.v. −3,290 (*Th.*). *Critical temperature*, 13°. S. ·25 at 0°; S. (alcohol) 3·6 at 0° (Carius, *A.* 94, 133). Discovered by treating alcohol with H_2SO_4 in 1795 by the four Dutch chemists: Deiman, Pæts van Troostwyk, Bondt, and Lauwerenburgh (*Crell. Ann.* 1795, ii. 195, 310; *Gilb. Ann.* 2, 201). It is a product of the dry distillation of most organic bodies, *e.g.* formates, acetates, butyrates, fats, resins, caoutchouc, wood, and coal. It is the most abundant illuminating constituent in coal gas.

Formation.—1. Formed, as well as other hydrocarbons, when a mixture of CS_2 and H_2S or H_3P is passed over red-hot copper; or, more abundantly, when a mixture of CS_2, H_2S, and CO is passed over red-hot iron (Berthelot, *C. R.* 43, 236).—2. Formed together with CH_4 and butylene by the dry distillation of barium formate.—3. By heating a mixture of alcohol (1 vol.) with conc. H_2SO_4 (4 vols.) (Mitscherlich, *A. Ch.* [3] 7, 12).—4. By heating alcohol (1 pt.) with fused B_2O_3 (4 pts.) (Ebelmen, *A. Ch.* [3] 16, 136). 5. By the electrolysis of a concentrated solution of sodium succinate (Kekulé, *A.* 131, 79).—6. Together with benzene, by heating styrene with hydrogen in sealed tubes (Berthelot, *J.* 1866, 544).—7. By treating ethylidene chloride with sodium (Tollens, *A.* 137, 311).—8. From ethyl iodide and zinc (E. Frankland a. L. Dobbie, *C. J.* 33, 545).

Preparation. — Alcohol (25 g.) and H_2SO_4 (150 g.) are heated in a flask to 165°, and a mixture of alcohol (1 pt.) and H_2SO_4 (2 pts.) is run in slowly. The gas is washed with NaOHAq and H_2SO_4 (Erlenmeyer a. Bunte, *A.* 168, 64; 192, 244).

Properties.—Colourless gas with faint ethereal odour (?). V. sl. sol. water, sl. sol. alcohol, m. sol. ether. Pure ethylene burnt at the rate of 5 cubic feet per hour emits a light equal to 68·5 standard candles; the illuminating power of a given quantity of C_2H_4 is increased by moderate admixture with H, CO, or CH_4, although the actual amount of light given per cubic foot of the mixture is less than that given by pure ethylene. The intrinsic illuminating power is reduced by admixture with N, CO_2, or water-vapour, but increased by O (P. F. Frankland, *C. J.* 45, 30, 227). It unites directly with chlorine, bromine, iodine, N_2O_4, S_2Cl_2, and SO_3. It is quickly absorbed by Nordhausen sulphuric acid, forming ethionic acid and its anhydride. Conc. H_2SO_4 absorbs it, forming $HEtSO_4$; the absorption takes place rapidly at 100°–170°, but at ordinary temperature much shaking is required. Ethylene forms with water under pressure a crystalline hydrate (Villard, *C. R.* 106, 1602).

Reactions.—1. When passed through a *red-hot tube* carbon is deposited and marsh-gas formed. The decomposition commences at as low a temperature as 355°; at this temperature a condensation change only takes place, and is very slow, requiring 20 hours or more for its completion. Heated to 400° for a sufficient length of time it is entirely decomposed with formation of marsh-gas, ethane, and liquid products (Day, *Am.* 8, 153). According to Berthelot (*Bl.* [2] 9, 456) these liquid products contain benzene and styrene. Norton a. Noyes (*Am.* 8, 362) found benzene, naphthalene, and anthracene, as well as methylene, propylene, butylene, and crotonylene, $CH_2{:}CH.CH{:}CH_2$, with CH_4, and C_2H_6. When heated in a glass tube to dull redness with an equal volume of acetylene it appears to form butylene (Berthelot, *J.* 1866, 519). When a mixture of ethylene and hydrogen is passed over platinum, even in the cold, ethane is formed (Von Wilde, *B.* 7, 352). A mixture of ethylene and diphenyl passed through a red-hot porcelain tube forms phenanthrene, anthracene, benzene, styrene, and naphthalene (Barbier, *C. R.* 79, 121). 2. With *oxygen* (3 vols.) it forms a highly explosive mixture. When a mixture of ethylene and air is passed over red-hot platinum wire some acetic acid is formed (Coquillion, *C. R.* 77, 444). When ethylene is oxidised by weakly-ozonised oxygen, formic acid and CO_2 result (Houzeau a. Renard, *C. R.* 76, 572).—3. It burns in *chlorine* with a smoky flame:

$$C_2H_4 + 2Cl_2 = 2C + 4HCl.$$

In the dark and in the cold it unites with chlorine, forming oily 'Dutch liquid' $C_2H_4Cl_2$.—4. HI at 100° forms EtI (Berthelot, *A.* 104, 184; 115, 114; *J.* 1867, 344). HBr also unites with ethylene, but HCl does not.—5. Dry ICl forms $C_2H_4Cl_2$ and iodine (Geuther, *J.* 1862, 421; Thorpe, *C. J.* 37, 179).—6. *Chromic acid* solution oxidises it to CO_2 (Ludwig, *A.* 162, 47). Chromic acid mixture forms chiefly oxalic and acetic acids (Zeidler, *A.* 197, 243); Berthelot (*C. R.* 68, 334) found even aldehyde.—7. *Potassium permanganate* solution containing H_2SO_4 is decolourised by ethylene, CO_2 and formic and acetic acids being formed. Neutral and alkaline $KMnO_4$ forms chiefly oxalic acid and CO_2, together with a little formic acid (Zeidler; Truchot, *C. R.* 63, 274; Berthelot, *C. R.* 64, 35). Neutral $KMnO_4$ solution forms also glycol (Wagner, *B.* 21, 1230). 8.—Fuming HNO_3 absorbs it, forming oxalic acid.—9. $ClSO_3H$ absorbs dry ethylene with rise of temperature; at 90° isethionic anhydride $C_2H_4SO_3$ is formed, but if the sulphuric chlorhydrin be kept cool and the product poured into water an oil, $C_2H_5SO_3Cl$ (154°), smelling like mustard oil, is obtained; this oil is converted by water at 100° into isethionic acid, and by dry NH_3 into deliquescent tables of $C_2H_7NSO_3$ (Baumstark, *Z.* 1867, 566).—10. *Boron fluoride* at 30° in sunlight forms $C_2H_3BF_2$, an ethereal liquid (125°) S.G. $\underline{23}$ 1·0478, V.D. 2·55, which fumes in the air. It is decomposed by water into ethylene, H_3BO_3, and HF (Landolph, *C. R.* 86, 671, 1267; 89, 173). This 'fluoboro-ethylene' acting upon camphor at 200° forms a hydrocarbon $C_{12}H_{18}$.—11. Ethylene and HBr passed over Al_2Br_6 form $AlBr_3C_4H_8$, and ethyl bromide. C_2H_4, HCl, and Al_2Cl_6 give $AlCl_3C_4H_8$ (Gustavson, *J. pr.* [2] 34, 161). At the same time saturated hydrocarbons are formed—very little at 0°, much at 70°; they are formed by the simultaneous action of C_2H_4 and HBr on $AlBr_3C_4H_8$. Ethyl bromide at 60° acts like C_2H_4 mixed with HBr. $AlBr_3C_4H_8$ gives saturated hydrocarbons, not only with C_2H_4 and HBr, but also with EtBr, PrBr, isobutyl bromide, and MeBr. In all these cases the $AlBr_3C_4H_8$ becomes richer in carbon.—12. *Chloride of sulphur* forms $S_2(CH_2.CH_2Cl)_2$ (Guthrie, *A.* 119, 91; 121, 108; Spring a. Lecrenier, *Bl.* [2] 48, 629).—13. Cl_2O forms chiefly $CH_2Cl.CO.O.CH_2.CH_2Cl$ (chloro-ethyl chloro-acetate (Mulder a. Bremer, *B.* 11, 1958).—14. HClO forms $CH_2Cl.CH_2OH$ (Carius, *A.* 126, 197).—15. A solution of $PtCl_2$ in conc. HClAq forms $C_2H_4PtCl_2$ (Birnbaum, *A.* 145, 69). The same compound is formed by boiling $PtCl_4$ with alcohol (Zeise, *P.* 21, 497, 542; 40, 234; Griess a. Martius, *Pr.* 11, 509). It is a yellow mass, sl. sol. water; decomposed by light. In aqueous solution it is unstable unless HCl is present. KOH ppts. on warming an explosive powder. It forms the following combinations: $NH_3C_2H_4PtCl_2$: yellow pp.—$NH_4ClC_2H_4PtCl_2$ aq: lemon-yellow prisms.—$KClC_2H_4PtCl_2$ aq.—$KBrC_2H_4PtBr_2$aq: pale-yellow needles (Chojnacki, *Z.* 1870, 421).—$C_2H_4Pt_2Cl_4(Et_3PO_3)_2$ (Schützenberger, *Bl.* [2] 18, 103). The corresponding $NH_4ClC_2H_4IrCl_2$ and $(KClC_2H_4)_2IrCl_2$ may also be prepared (Sadtler, *Bl.* [2] 17, 54).—16. When ethylene is passed into conc. aqueous $FeBr_2$ in sunlight there are formed greenish deliquescent crystals of $C_2H_4FeBr_2$ 2aq (Chojnacki). The corresponding $C_2H_4FeCl_2$ 2aq is got by heating ether (50 g.) with Fe_2Cl_6 (5 g.), P ($\frac{1}{5}$ g.) and CS_2 ($\frac{2}{5}$ g.) at 100° (Kachler, *B.* 2, 510).

Derivatives of ethylene: *v.* Bromo-, Bromo-nitro-, Bromo-iodo-, Chloro-, Chloro-nitro-, Chloro-iodo- &c. ethylene.

ETHYLENE-ACETOACETIC ACID *v.* Aceto-acetic acid.

ETHYLENE ALCOHOL *v.* Glycol.

ETHYLENE-ORTHALDEHYDE *v.* Aldehyde.

ETHYLENE-DI-ALLYL-DI-THIO-DI-UREA $C_2H_4(NH.CS.NHC_3H_5)_2$. From ethylene-diamine and allyl thiocarbimide (mustard oil) in alcohol. Brownish oil, miscible with chloroform and with alcohol. Has an unpleasant odour (Lellmann a. Würthner, *A.* 228, 234)

ETHYLENE-DI-*m*-AMIDO-DIBENZOIC ACID $C_2H_4(NH.C_6H_4.CO_2H)_2$. [222°–225°]. From ethylene bromide and *m*-amido-benzoic acid by boiling 24 hours in alcoholic solution (Schiff a. Parenti, *A.* 226, 244). Hardly sol. water, sol. boiling alcohol. Insol. dilute HCl, sol. aqueous NaOH. With KOH (4 mols.) and EtI (6 mols.) it forms needles of $C_{24}H_{32}N_2O_4$ [100°].

Salt.—CuA″aq.

ETHYLENE-DI-β-AMIDO-DI-(α)-CROTONIC ACID $C_{10}H_{16}N_2O_4$ *i.e.* $C_2H_4(NH.CMe:CH.CO_2H)_2$. [168°]. Obtained by saponification of the ether or by heating ethylene diamine with three times its weight of acetoacetic ether for an hour at 140°. White silky scales. V. sol. water and hot alcohol, sl. sol. ether, benzene, and cold alcohol. Gives a violet colouration with Fe_2Cl_6.

Di-ethyl ether A″Et_2: [127°]; obtained by mixing ethylene-diamine and acetacetic ether in aqueous or alcoholic solution; large white prisms; sol. hot alcohol, ether, and benzene, sl. sol. these solvents when cold, insol. water; conc. HCl decomposes it into acetacetic ether and ethylene-diamine (Mason, *B.* 20, 273).

ETHYLENE-DIAMINE $C_2H_8N_2$ *i.e.* $NH_2.CH_2.CH_2.NH_2$. Mol. w. 80. [8°]. (117°). V.D. 2·00 (calc. 2·08). S.G. $\underline{15}$ ·902.

Formation.—1. From ethylene bromide and alcoholic ammonia in the cold (Hofmann, *Pr.* 9, 154; 10, 224; *cf.* Cloez, *J.* 1853, 468).—2. From ethylene chloride and alcoholic NH_3 (20 mols.) (Lellmann a. Würthner, *A.* 228, 226). The fraction (70°–100°) from the preparation of chloral contains ethylene and ethylidene chlorides, and if it be heated with alcoholic NH_3 at 110° for 9 hours, the ethylene chloride is converted into the diamine, while the ethylidene chloride is not affected (Hofmann, *B.* 4, 666).—3. From chloro-ethylene and NH_3 at 160° (Engel, *Bl.* [2] 48, 96).—4. By reducing cyanogen with tin and HCl (Fairley, *A. Suppl.* 3, 372).

Preparation.—A nearly theoretical yield of the hydrochloride is obtained when ethylene chloride (42 g.) is heated in a sealed tube to 115°–120° with 33 p.c. aqueous ammonia (510 c.c.). The crystals are washed with absolute alcohol until the washings cease to colour Nessler's solution. The alcohol yields a fresh crop of crystals containing ammonium chloride and di-ethylene-diamine hydro-chloride. The hydrate of the free base is obtained by the addition of freshly fused and powdered caustic soda to the chloride, then adding soda-lime and distilling. The anhydrous base is obtained from this hydrate by again heating with fused soda in a sealed tube for several hours (Kraut, *A.* 212, 254).

Properties.—Volatile alkaline liquid; it is very difficult to dry, requiring treatment with sodium. V. sol. water. It forms a hydrate B″aq [10°] (118°). S.G. $\underline{15}$ ·970, not miscible with benzene or ether.

Reactions.—1. *Nitrous acid* forms nitrogen and ethylene oxide.—2. EtI forms $C_2H_4N_2H_4Et_2I_2$ whence $C_2H_4N_2H_2Et_2$ aq, which is in turn converted by EtI into $C_2H_4N_2H_2Et_4I_2$, whence moist Ag_2O yields a volatile base whence $C_2H_4N_2HEt_5I_2$ and $C_2H_4N_2Et_6I_2$ may be obtained. The two last iodides when treated with moist Ag_2O leave fixed bases. $C_2H_4N_2Me_6I_2$ has also been prepared. The compound $C_2H_4N_2Et_4H_2Br_2$ may also be obtained from ethylene-diamine and di-ethylamine (Hofmann, *Pr.* 11, 423); it gives $C_2H_4N_2Et_4(HAuCl_4)_2$. $C_2H_4N_2H_4Et_2Br_2$ is one of the products of the action of ethylamine on $C_2H_4Br_2$; the corresponding base $C_2H_4N_2H_2Et_2$aq crystalline; it may be dehydrated by repeated distillation over baryta, when its V.D. (H = 1) is 57·61 (calc. 58). The hydrated base $C_2H_4N_2H_2Et_2$ aq has a V.D. 33·2, showing dissociation (Hofmann, *Pr.* 10, 597). By cohobating equal mols. of *benzil* and *ethylene-diamine hydrate* for ⅓ hour, a base $C_{16}H_{14}N_2$ possibly

$$\begin{array}{c} C_6H_5.C=N.CH_2 \\ \vert \qquad\quad \vert \\ C_6H_5.C=N.CH_2 \end{array}$$

is formed [161°]. Yellowish prisms. V. sol. ether, benzene, and hot alcohol, sparingly in cold alcohol, insol. water. By hot conc. mineral acids it is split up into ethylene diamine and benzil (Mason, *B.* 20, 268).—4. CS_2 in presence of alcohol forms $C_2H_4N_2H_4CS_2$ which may be crystallised from water. Boiling aqueous $HgCl_2$ converts it into ethylene thio-urea (Hofmann, *B.* 5, 241).—5. ***Pyrocatechin*** heated with ethylene-diamine hydrate at 205° forms $C_6H_4<{NH \atop NH}>C_2H_4$ [97°] (Merz a. Ris, *B.* 20, 1190).—6. *Benzoic aldehyde* at 120° forms di-benzylidene-ethylene diamine $(PhCH:N)_2C_2H_4$ [54°] (Mason, *B.* 20, 270). Substituted benzoic aldehydes act in the same way.—7. When ethylene diamine hydrochloride is heated it is partly converted into ethylene-imine C_2H_4NH (Ladenburg a. Abel, *B.* 21, 758).—8. *Hexa-chloro-acetone* forms $C_2H_4N_2H_4C_2Cl_4O$ [200°]. *Penta-chloro-acetone* forms $C_2H_4N_2H_4C_2HCl_2O$ which crystallises from ether in fan-shaped plates (Cloëz, *A. Ch.* [6] 9, 145).—9. *Carbonic ether* at 180° forms white needles of ethylene-urea $C_2H_4<{NH \atop NH}>CO$. [131°] (Fischer a. Koch, *A.* 232, 227).—10. *Di-methyl-methylene diketone* CH_2Ac_2 forms a solid $C_{12}H_{10}N_2O_2$ [111°], which forms a violet copper salt [137°], and a hydrochloride $B''H_2Cl_2$ (Combes, *Bl.* [2] 50, 517).

Salts.—$B''H_2Cl_2$: long silvery needles, insol. alcohol.—$B''H_2PtCl_6$: yellow plates (Griess a. Martius, *A.* 120, 327).—$B''(HSCy)_2$: [c. 145°]; prisms, v. e. sol. water, v. sol. alcohol, insol. ether. Split up by heat into ammonium sulphocyanide and ethylene thio-urea (Hofmann, *A.* 70, 143).—**Sulphate**: dimetric crystals (Von Lang, *C. C.* 1872, 178).

Di-formyl derivative $C_2H_4N_2H_2(CHO)_2$. From ethylene-diamine and chloral. Syrup (Hofmann, *B.* 5, 240).

Di-acetyl derivative $C_2H_4(NHAc)_2$. [172°]. Colourless needles. Sl. sol. ether. Forms a crystalline aurochloride $B'HAuCl_4$ and platino-chloride $B'_2H_2PtCl_6$. When heated in a current of dry HCl it forms ethylene acetamidine $C_2H_4<{N \atop NH}\geqslant CMe$ [88°] (223°), of which the aurochloride $B'HAuCl_4$ and platino-chloride $B'_2H_2PtCl_6$ are crystalline (Hofmann, *B.* 21, 2332).

Benzoyl derivative $C_2H_4N_2H_2Bz_2$. [249°] (Kraut a. Schwartz, *A.* 223, 43). S. (alcohol) ·076 at 22°. Needles (from alcohol). Insol. water. When heated in a current of dry HCl it forms ethylene-benzamidine $C_2H_4<{N \atop NH}\geqslant CPh$ [101°], of which the salts $B'HAuCl_4$ and $B'_2H_2PtCl_6$ are crystalline (Hofmann).

Di-ethylene-diamine $C_4H_{10}N_2$ *i.e.* $NH<{C_2H_4 \atop C_2H_4}>NH$. (c. 170°). V.D. 2·7 (calc. 2·9). Formed, together with ethylene-diamine and tri-ethylene-diamine by the action of ethylene chloride on alcoholic ammonia (Hofmann; Natanson, *A.* 98, 291). Alternate treatment with EtI and moist silver oxide yields three bases, one volatile and two fixed. The corresponding iodides are $(C_2H_4)_2N_2H_2Et_2I_2$, $(C_2H_4)_2N_2HEt_3I_2$, and $(C_2H_4)_2N_2Et_4I_2$. MeI forms $(C_2H_4)_2N_2Me_4I_2$. By the action of ethylene bromide on ethylamine there is formed $(C_2H_4)_2N_2H_2Et_2Br_2$, as well as $C_2H_4N_2H_4Et_2Br_2$. On distilling the former with baryta the free base $(C_2H_4)_2N_2Et_2$ (185°) is obtained.

Tri-ethylene-diamine $C_6H_{12}N_2$ *i.e.* $(C_2H_4)_3N_2$. Mol. w. 112. (c. 210°). Formed by the action of NH_3 on ethylene chloride (Hofmann, *Pr.* 10, 104).

Di-ethylene-triamine $C_4H_{13}N_3$ *i.e.* $NH(C_2H_4NH_2)_2$. (208°). The bromide $(C_2H_4)_2N_3H_8Br_3$ is among the products of the action of ammonia on ethylene bromide (Hofmann). The portion of the bases boiling from 200° to 220° consists almost wholly of di- and tri- ethylene-triamine, which may be separated by crystallisation of their platinochlorides. Strongly alkaline liquid, miscible with water and alcohol, almost insol. ether. Neutralises acids completely, giving beautifully crystallised salts, generally v. sol. water, sl. sol. alcohol, insol. ether. The aqueous solution is not ppd. by KOHAq, but solid KOH causes the base to separate as a liquid layer, which rapidly absorbs CO_2 from the air.—$B'''H_3Cl_3$.—$B'''H_2Cl_2$.—$B'''_2 3H_2PtCl_6$: golden needles; cannot be recrystallised without decomposition.—$B'''H_2PtCl_6$.—$B'''_2H_2PtCl_6$.—$B'''HClH_2PtCl_6$.—$B'''_2H_4Cl_4H_2PtCl_6$.

Among the products of the action of ethylamine on ethylene bromide are salts of the ethylated di-ethylene triamines $(C_2H_4)_2N_3H_3Et_2$ and $(C_2H_4)_2N_3H_2Et_3$, which boil at about 220° to 250°, and of which Hofmann (*Pr.* 11, 420) has prepared the following salts: $(C_2H_4)_2N_3H_6Et_2Cl_3$: nacreous leaves; differs from the hydrochlorides of related bases in being insol. alcohol.—$(C_2H_4)_2N_3H_5Et_2I_2$. $(C_2H_4)_2N_3H_6Et_2I_3$: deposited only when excess of hydric iodide is present.—$(C_2H_4)_2N_3H_3Et_2 3HNO_3$.—**Platinochloride** $\{(C_2H_4)_2N_3H_2Et_3\}_2 3H_2PtCl_6$. The formation of $(C_2H_4)_2N_3H_3Et_2$ must be ascribed to the presence of NH_3 in the ethylamine used.

Tri-ethylene-triamine $(C_2H_4)_3N_3H_3$. (216°). Formed as above. Its triacid salts are only formed in presence of a large excess of acid, feebly acid solutions depositing salts with 1 or 2 equivalents of acid.—$B'''_2 3H_2PtCl_6$: long golden needles, more soluble in water than the platinochlorides of di-ethylene-triamine and of the ethylene-diamines. Decomposed by recrystallisation.—$B'''3HAuCl_4$: yellow plates, sol. water, alcohol, and ether; may be recrystallised from water, but decomposed by long boiling therewith, gold being ppd.—$B'''H_2Br_2$.

The ethylated derivative $(C_2H_4)_3N_3Et_3$ is an alkaline oil, boiling between 220° and 250°, formed by the action of ethylamine on ethylene bromide; it forms a platinochloride $B'''_2 3H_2PtCl_6$.

Tetra-ethylene-triamine $(C_2H_4)_4N_3H$. A mixture of the hydrobromides of this base appears to be deposited when ethylene bromide is mixed with alcoholic NH_3 and left to itself for several months (Hofmann, *B.* 3, 762). Combines with 1, 2, or 3 equivalents of HBr forming amorphous salts, insol. water, alcohol, and ether. By prolonged boiling with ammonia the corresponding hydroxides are got in an amorphous uncrystallisable form, insol. water, alcohol, and ether.

Tri-ethylene-tetramine $(C_2H_4)_3N_4H_6$. Occurs among the products of the action of ethylene bromide on ammonia, but is best obtained pure by treating ethylene-diamine with $C_2H_4Br_2$, and separated from its hydrobromide by moist Ag_2O. Strongly alkaline liquid.—$B''2H_2PtCl_6$: pale yellow, amorphous, powder, almost insol. water. By the action of diethylamine on ethylene bromide at 100° there is formed $(C_2H_4)_3N_4Et_8H_2Br_4$, together with the compound $(C_2H_4)N_2Et_4H_2Br_2$ already mentioned. If the mixture be treated with Ag_2O and the liberated bases distilled with steam the volatile diethylamine and tetra-ethyl-ethylene-diamine pass off, while the fixed octo-ethyl-tri-ethylene tetrammonium hydroxide $(C_2H_4)_3N_4Et_8H_2(OH)_4$ remains behind. It forms the following salts: $(C_2H_4)_3N_4Et_8H_2Cl_42PtCl_4$: small crystalline plates, almost insol. water.—$(C_2H_4)_3N_4Et_8H_2Cl_44AuCl_3$. — $(C_2H_4)_3N_4Et_8H_2I_4$: white crystals (from alcohol); v. sol. water. Further treatment with EtI gives $(C_2H_4)_3N_4Et_9HI_4$, which forms very fine crystals; m. sol. alcohol.

Penta-ethylene tetramine $(C_2H_4)_5N_4H_2$. When ethylene bromide is heated with ethylamine to 100° the following products result, besides $NEtH_3Br$: $C_2H_4N_2Et_2H_4Br_2$—$(C_2H_4)_2N_2Et_2H_2Br_2$ — $(C_2H_4)_2N_3Et_3H_5Br_3$ — $(C_2H_4)_3N_3Et_3H_3Br_3$ — $(C_2H_4)_5N_4Et_4H_2Br_4$—$(C_2H_4)_6N_4Et_4Br_4$. The bases corresponding to the first four salts have already been mentioned as being volatile. The product is therefore treated with moist Ag_2O and then distilled with steam; the residual liquid is powerfully alkaline and consists chiefly or altogether of $(C_2H_4)_5N_4Et_4H_2(OH)_4$. The salts of this base crystallise with difficulty. Hofmann describes $(C_2H_4)_5N_4Et_4H_2Cl_42PtCl_4$ and the aurochloride $(C_2H_4)_5N_4Et_4H_2Cl_44AuCl_3$ as amorphous or indistinctly crystalline and sl. sol. water. EtI forms $(C_2H_4)_5N_4Et_5HI_4$ and $(C_2H_4)_5N_4Et_6I_4$.

Hexa-ethylene tetramine $(C_2H_4)_6N_4$. The ethylo-bromide $(C_2H_4)_6N_4Et_4Br_4$ is formed as above, but is better prepared by the action of ethylene bromide on $C_2H_4N_2Et_2H_2$ or $(C_2H_4)_2N_2Et_2$.

ETHYLENE DIISOAMYL DISULPHIDE $C_2H_4(SC_5H_{11})_2$. (245°–255°). From ethylene bromide and sodium isoamyl mercaptan (Ewerlöf, *B.* 4, 716). Gives $C_2H_4(SOC_5H_{11})_2$ [145°–150°] on oxidation.

ETHYLENE-ANILINE *v.* DI-PHENYL-ETHYLENE-DIAMINE.

ETHYLENE-BENZOATE *v. Benzoyl derivative of* GLYCOL.

ETHYLENE-DI-BENZOYL CARBOXYLIC ACID *v.* DI-PHENYL-ETHYLENE DIKETONE CARBOXYLIC ACID.

ETHYLENE-BENZYL-CARBOXYLIC ACID *v.* DI-PHENYL-BUTANE DI-CARBOXYLIC ACID.

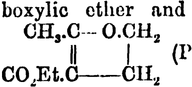
ETHYLENE BROMIDE $C_2H_4Br_2$ *i.e.* $CH_2Br.CH_2Br$. *Di-bromo-ethane.* [9·2°]. (131½° cor.). S.G. $\frac{15}{15}$ 2·1890; $\frac{25}{25}$ 2·1720 (Perkin); $\frac{21.5}{4}$ 2·1767; $\frac{10.9}{4}$ 2·1901 (Thorpe, *C. J.* 37, 177); $\frac{20}{4}$ 2·1768 (Weegmann, *Z. P. C.* 2, 218). C.E. (0°–10°) ·00096; (0°–100°) ·001061. V.D. 6·49 (calc. 6·56). M.M. 9·700 at 15·2° (Perkin, *C. J.* 45, 522). S.V. 91·65 (Schiff); 97·06 (Thorpe).

Formation.—1. By combination of bromine with ethylene (Balard, *A. Ch.* [2] 32, 375; Löwig, *Das Brom*, Heidelberg, 1829; Serullas, *A. Ch.* [2] 39, 228; D'Arcet, *J. pr.* 5, 28; Regnault, *A. Ch.* [2] 59, 358; Hofmann, *C. J.* 13, 67).—2. By bromination of ethyl bromide in presence of Al_2Br_6 (Tavildaroff, *B.* 6, 1459; 13, 2403; *Bl.* [2] 34, 316).

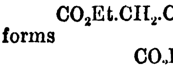
Preparation.—Ethylene is passed through a series of bottles containing bromine covered by water; the product is washed with alkali, dried with $CaCl_2$, and distilled (Erlenmeyer a. Bunte, *A.* 168, 64).

Properties.—Colourless liquid with pleasant smell; below 9° it is a crystalline mass. Insol. water, sol. alcohol and ether.

Reactions.—1. *Alcoholic potash* on boiling gives vinyl bromide and acetylene.—2. KHS forms $C_2H_4(SH)_2$.—3. K_2S gives C_2H_4S and $C_2H_4S_2$.—4. AgOAc produces $C_2H_4(OAc)_2$.—5. Alcoholic KOAc forms $C_2H_4(OH)(OAc)$.—6. KCy forms $C_2H_4(CN)_2$.—7. *Ammonia* forms ethylene-diamine, di-ethylene-diamine, tri-ethylene-diamine, &c.—8. *Water* at 160° forms aldehyde (Carius, *A.* 131, 172); Kriwaxin (*Z.* [2] 7, 263) obtained no aldehyde. But when excess (26 pts.) of water is used at 100° glycol is formed (Niederist, *A.* 196, 354). Water and PbO at 220° form aldehyde (Eltekoff, *B.* 6, 558; Nevole, *B.* 9, 447).—9. *Alcohol* at 160° gives water, aldehyde, ethyl bromide, and ether (Carius).—10. Fuming H_2SO_4, SO_3 or $ClSO_3H$ at 100° form $CH_2Br.CH_2.SO_3H$ (Wroblewsky, *Z.* [2] 4, 563; 5, 281).—11. Reduced in presence of water or alcohol by *zinc* slowly, but more quickly by the *copper-zinc couple*, the product being ethylene (Gladstone a. Tribe, *C. J.* 27, 106). Ethylene is also formed by heating $C_2H_4Br_2$ with aqueous KI.—12. Water and Ag_2CO_3 form glycol. Water and Ag_2O give aldehyde (Beilstein a. Wiegand, *B.* 15, 1368).—13. Ag_2SO_4 in benzene forms $(CH_2Br.CH_2)_2SO_4$. Ag_2SO_4 in water gives $(CH_2Br.CH_2)SO_4H$ (B. a. W.).—14. Ethylene bromide (188 g.) boiled with water (1,000 g.) and KOH (112 g.) is completely converted (in 6 hours) into KBr and vinyl bromide (Stempnewsky, *A.* 192, 210).—15. Boiling with dilute Na_2CO_3 forms glycol.—16. Boiled with aqueous sodium sulphite it probably forms sodic isethionate, thus: $C_2H_4Br_2 + Na_2SO_3 + H_2O = HO.C_2H_4.SO_3Na + NaBr + HBr$ (James, *C. J.* 43, 44), as well as ethane di-sulphonic acid (Strecker, *A.* 148, 90).—17. $SbCl_5$ forms $CH_2Cl.CH_2Br$ (Henry, *C. R.* 97, 1491).—18. Et_2S forms EtBr, $(C_2H_4)_2S_2$, Et_3SBr, and perhaps $(C_2H_4)_2S_2EtBr$ (Dehn, *A. Suppl.* 4, 83; *B.* 2, 479; Masson, *C. J.* 49, 253).—19. Fuming HNO_3 forms bromo-acetic acid and $CBr_2(NO_2)_2$ (Kachler, *M.* 2, 559).—20. Boiling conc. HIAq forms ethylene iodide (Sorokin, *Z.* 1870, 519).—21. With *sodium-aceto-acetic ether* it gives

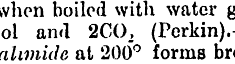


, acetyl-trimethylene carboxylic ether and very small quantities of



(Perkin, jun., *C. J.* 51, 822).

22. *Di-sodium acetone di-carboxylic ether* forms



. The resulting acid when boiled with water gives acetyl-propyl alcohol and $2CO_2$ (Perkin).—23. *Potassium phthalimide* at 200° forms bromo-ethyl-phthalimide $C_6H_4C_2O_2N.C_2H_4Br$ which when heated with concentrated hydric bromide at 190°

forms the hydrobromide of bromo-ethylamine $CH_2Br.CH_2.NH_3Br$ [155°–160°]. Diluted H_2SO_4 decomposes bromo-ethyl-phthalimide forming oxyethylamine $CH_2OH.CH_2NH_2$ (Gabriel, *B.* 21, 566).

ETHYLENE BROMO-IODIDE *v.* BROMO-IODO-ETHANE.

ETHYLENE CARBAMATE $C_2H_4(OCONH_2)_2$. [149°]. Formed by the action of chloro-formic amide on glycol, the later being in excess (Gattermann, *A.* 244, 42). Crystalline flocculent mass. Sl. sol. ether, CS_2, v. sol. hot water, alcohol, HOAc.

ETHYLENE DI-CARBAMIC ETHER $C_2H_4(NH.CO.OC_2H_5)_2$. *Ethylene diurethane.* [112°]. Prepared by adding ethylene-diamine to an ethereal solution of ethyl chloro-carbonate and purified by distillation under 30 mm. Colourless needles. V. sol. alcohol and ether, v. sl. sol. water (Fischer a. Koch, *A.* 232, 228).

ETHYLENE CARBONATE $C_2H_4CO_3$. [39°]. (236°). From glycol and $COCl_2$ (Nemirowsky, *J. pr.* [2] 28, 439). Needles (from ether). V. sol. water, alcohol, and warm ether.

ETHYLENE DI-CARBOXYLIC ACID *v.* FUMARIC ACID.

Ethylene tetra-carboxylic acid $C_6H_4O_8$ *i.e.* $(CO_2H)_2C:C(CO_2H)_2$. The free acid decomposes very readily.

Salts.—K_2H_2A'''': from the ether by conc. KOHAq.– Ca_2A'''' 7aq.—Ag_4A''''.

Ethyl ether Et_4A''''. [58°]. (325°–328°). Formed by the action of NaOEt on chloro-malonic ether (Conrad a. Guthzeit, *A.* 214, 76). Formed also by the action of iodine (2 mols.) on di-sodio-malonic ether (2 mols.) in absolute alcohol (Bischoff a. Rach, *B.* 17, 2781). Monoclinic tables. V. e. sol. ether or boiling alcohol, insol. water. Does not combine with bromine. Prepared by digesting chloro-malonic ether, diluted with anhydrous ether, for 20 hours with sodium; yield 50 p.c. of the theoretical. By heating with alcohol and aqueous HCl to 190° it yields fumaric acid. By zinc-dust and HCl it is reduced to ethane tetra-carboxylic acid (Conrad a. Guthzeit, *B.* 16, 2631).

ETHYLENE CHLORHYDRIN *v.* CHLORO-ETHYL ALCOHOL.

ETHYLENE CHLORIDE $C_2H_4Cl_2$ *i.e.* $CH_2Cl.CH_2Cl$. *Di-chloro-ethane.* Mol. w. 99. (83·6°) (Thorpe, *C. J.* 37, 182); (83·7° cor.) (Perkin, *C. J.* 45, 528). V.D. 3·42 (calc. 3·42). S.G. $\frac{0}{4}$ 1·2808 (Th.); $\frac{9.8}{4}$ 1·2656 (Schiff, *A.* 220, 96); $\frac{20}{4}$ 1·2521 (Brühl, *A.* 203, 10); 1·2501 (Weegmann, *Z. P. C.* 2, 218); $\frac{15}{15}$ 1·2599; $\frac{25}{25}$ 1·2480 (P.). C.E. (0°–10°) ·001162; (0°–50°) ·001218 (T.); (9·8° to 83·3°) ·001269 (S.). S.V. 85·34 (Thorpe); 87·2 (Ramsay); 85·24 (Schiff). M.M. 5·485 at 14·4° (Perkin). μ_D 1·144 (W.). μ_β 1·4502. R_∞ 34·12 (B.). H.F.p. 34,280 (Th.). H.F.v. 33,120 (Th.).

Discovered in 1795 by the four Dutch chemists (*v.* ETHYLENE) and hence called 'Dutch liquid.' Produced by admitting ethylene and moist chlorine simultaneously into a large globe. It may also be prepared by passing ethylene through a slightly heated mixture of MnO_2 (2 pts.), NaCl (3 pts.), water (4 pts.), and H_2SO_4 (5 pts.). Formed also by passing ethylene into $SbCl_5$. The product obtained from any one of these reactions is washed with alkali, dried over $CaCl_2$, and rectified (Liebig, *A.* 1, 213; 9, 20; Dumas, *A. Ch.* [2] 48, 185; Wöhler, *P.* 13, 297; Laurent, *A. Ch.* [2] 63, 377; Regnault, *A. Ch.* [2] 58, 301; 69, 251; 71, 371; Limpricht, *A.* 94 245; Malaguti, *A. Ch.* [3] 16, 6, 14; Pierre, *C. R.* 25, 430). It is formed also by heating glycol with excess of HCl in sealed tubes at 100° (Schorlemmer, *C. J.* 39, 144). It is obtained in large quantity, together with some of its chlorinated derivatives, from the by-products in the manufacture of chloral (Krämer, *B.* 3, 257).

Properties.—Oil, with sweetish odour; sol. alcohol and ether. Dissolves phosphorus. Not affected by H_2SO_4 at 100°, but at 130° carbon is separated (Oppenheim, *B.* 2, 212). Burns with green flame. Ethylene chloride may be used with great advantage as an anæsthetic in operations on the eye (Dubois a. Roux, *Compt. rend. Soc. Biol.* 4, 584; *C. R.* 108, 191).

Reactions.—1. Its vapour passed through a *red-hot tube* forms carbon, naphthalene, chloride of carbon, &c.—2. When covered with water and exposed to sunshine it is decomposed, yielding HCl and acetic ether.—3. It is chlorinated by Cl in heat or light.—4. Dry *ammonia* does not act upon it, but when dissolved in water or alcohol it forms the various ethylene-amines (Robiquet a. Colin, *A. Ch.* [2] 1, 213; 2, 206).—5. *Potassium* attacks it violently, forming hydrogen, vinyl chloride, and other products.—6. Aqueous *potash* has little action, but alcoholic potash gives ethylene and vinyl chloride (Maumené, *C. R.* 68, 931).—7. KHS, K_2S, K_2S_2, and KCyS give the corresponding ethers of ethylene.—8. PCl_5 at 190° yields $CHCl_2.CH_2Cl$ (121°–133°) and $CHCl_2.CHCl_2$ (133°–146°) (Colson a. Gautier, *A. Ch.* [6] 11, 31).

ETHYLENE CHLORO-BROMIDE *v.* CHLORO-BROMO-ETHANE.

ETHYLENE CHLORO-IODIDE *v.* CHLORO-IODO-ETHANE.

ETHYLENE CHLORO-THIOCYANATE *v.* CHLORO-ETHYL SULPHOCYANIDE.

ETHYLENE CYANIDE *v. Nitrile of* SUCCINIC ACID.

ETHYL-DI-ETHYL-DI-AMIDO-DI-BENZOIC ACID. *Ethylether.* $C_2H_4(NEt.C_6H_4.CO_2Et)_2$. [98°–100°]. From $C_2H_4(NH.C_6H_4.CO_2H)_2$ by KOH and IEt (Schiff a. Parenti, *A.* 226, 246). Doubly refracting prisms (from alcohol). Insol. water.

ETHYLENE-ETHYL-AMINES *v. Ethyl derivatives of* ETHYLENE-AMINES.

ETHYLENE DIETHYL CARBONATE $C_2H_4(O.CO_2Et)_2$. (226°). From sodium glycol $C_2H_4(ONa)_2$ and $ClCO_2Et$ in ether (Wallach, *A.* 226, 82). Split up by long boiling into carbonic ether and ethylene carbonate.

ETHYLENE-ETHYL-PHOSPHINE *v.* ETHYL-PHOSPHINE.

ETHYLENE-DI-ETHYL DI-SULPHIDE ×$C_2H_4(SEt)_2$. (212°). Formed by adding ethylene bromide to a boiling solution of sodium mercaptide (1 pt.) in ether (3 pts.) (Ewerlöf, *B.* 4, 716 Beckmann, *J. pr.* [2] 17, 468). Decomposed by heat. Converted by EtI at 100° into SEt_3I and $C_2H_4S_2$ (Braun, *B.* 20, 2967).

ETHYLENE-DI-ETHYL DI-SULPHONE $C_2H_4(SO_2.Et)_2$. *Ethylene disulphinic ether.* [137°]. Formed by oxidising ethylene-di-ethyl di-sulphoxide with $KMnO_4$ (Ewerlöf; Beckmann, *J. pr.* [2] 17, 468). Also from sodium ethane sulphinate and ethylene bromide, and from sodium ethylene disulphinate and EtBr (Otto a. Casanova, *J. pr.* [2] 30, 172; 36, 433). Short needles, sol. hot water and alcohol, sl. sol. ether, benzene, $CHCl_3$, and conc. HNO_3. Not affected by reducing agents, PCl_5, or $KMnO_4$. Nascent hydrogen in alkaline solution converts it into sodium ethane-sulphinate and alcohol. Successive treatment with aqueous KOH and BzCl gives $SO_2Et.CH_2.CH_2.OBz$ [118°]. It is uncertain whether ethylene di-ethyl di-sulphone has the constitution $C_2H_4\{S(O_2).Et\}_2$, or whether it is not rather the ethyl ether of ethane disulphinic acid, under which it has also been described.

ETHYLENE-DI-ETHYL DI-SULPHOXIDE $C_2H_4(SOEt)_2$. [170°]. Got by oxidising ethylene-di-ethyl di-sulphide with HNO_3 (S.G. 1·2), neutralising, evaporating, and extracting with alcohol (Beckmann, *J. pr.* [2] 17, 468). White scales, sol. water and alcohol, insol. ether. Reduced by Zn and H_2SO_4, or by HI to the corresponding sulphide. Attacked by PCl_5. Reduces $KMnO_4$.

Combination.—With nitric acid it forms, on evaporation, an acid syrup $C_2H_4(SOEt)_2$, HNO_3.

ETHYLENE ETHYL DI-THIO-DI-CARBONATE *v.* ETHYL THIO-CARBONATES.

(α)-ETHYLENE-DI-ETHYL-DI-UREA $C_8H_{18}N_4O_2$ *i.e.* $C_2H_4(NEt.CO.NH_2)_2$. [124°]. From di-ethyl-ethylene-diamine, hydrobromide, and silver cyanate (Volhard, *Pr.* 11, 268; *A.* 119, 349). Flat needles (from alcohol). V. sol. cold water, v. e. sol. alcohol, insol. ether. Boiling KOHAq gives NH_3, CO_2, and $C_2H_4(NEtH)_2$.—$B'_2H_2PtCl_6$: orange grains, decomposed by hot water.

(β)-Ethylene-di-ethyl-di-urea $C_2H_4(NH.CO.NHEt)_2$. [201°]. From ethylene-diamine and cyanic ether (Volhard). Small needles, v. sol. hot, sl. sol. cold, water, v. sl. sol. alcohol. Decomposed by boiling KOHAq, giving ethylamine and ethylene diamine. Is not basic.

ETHYLENE GLYCOL *v.* GLYCOL.

ETHYLENE HEPTYLIDENE DIOXIDE $C_6H_{13}.CH\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle C_2H_4$. (c. 180°). Formed by heating heptoic aldehyde (1 vol.) with glycol (3 vols.) at 130° for 8 days (Lochert, *Bl.* [2] 48, 337, 716). Formed also by heating a mixture of heptoic aldehyde (œnanthol) (1 vol.), glycol (2 vols.), and HOAc (1 vol.). Liquid.

ETHYLENE-IMINE C_2H_5N *i.e.* $\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle NH$, or $C_4H_{10}N_2$ *i.e.* $\left\langle\begin{matrix}CH_2.NH.CH_2\\CH_2.NH.CH_2\end{matrix}\right\rangle$. [159°–163°]. V.D. 2·93. Formed by subliming ethylene-diamine hydrochloride (4 g.); the sublimate is dissolved in water and ppd. by potassio-bismuthic iodide, the pp. being then decomposed by KOH (Ladenburg a. J. Abel, *B.* 21, 758, 2706). Deliquescent porcelain-like mass. Its V.D. corresponds to the formula $C_4H_{10}N_2$, but when first prepared it is possibly C_2H_5N. Insol. ether, v. sol. alcohol; absorbs CO_2 from the air. The base is perhaps identical with spermine.

Salts.—C_2H_5NHCl: tables, v. sol. water, insol. alcohol.—$B'_2H_2PtCl_6$: yellow prisms.—$B'_3H_3I_3Bi_2I_6$: garnet-red plates, insol. cold water.—$B'HAuCl_4$: nacreous leaflets, decomposed by heating with water.—$B'_2H_2Cl_2 3HgCl_2$: clusters of quill-like groups of needles.

ETHYLENE IODIDE $C_2H_4I_2$ *i.e.* $CH_2I.CH_2I$. [82°].

Formation.—1. By direct combination of iodine and ethylene in sunshine (Faraday, *Ann. Phil.* 18, 118), or by heating to 60° (Regnault, *A. Ch.* [2] 59, 367).—2. One of the products formed when EtI is passed through a red-hot tube (E. Kopp, *J. Ph.* [3] 6, 110).—3. From glycol and cold HI.—4. By heating ethylene chloride with CaI_2 3½aq at 75° (Spindler, *A.* 231, 265; Van Romburgh, *R. T. C.* 1, 151).

Preparation.—A pasty mixture of iodine and absolute alcohol is saturated with ethylene and agitated, fresh quantities of iodine being added from time to time (Semenoff, *Zeit. Ch. Pharm.* 1864, 673).

Properties.—Colourless needles or prisms; may be readily sublimed in hydrogen or ethylene. Insol. water, v. sol. ether and boiling alcohol. Slowly split up, especially under the influence of light, into ethylene and iodine; this change takes place rapidly at 85°.

Reactions.—1. *Chlorine* gives iodine and ethylene chloride. *Bromine* acts in the same way.—2. Aqueous KOHAq has but little action; but boiling *alcoholic potash* gives ethylene and vinyl iodide.—3. *Water* at 275° gives ethane, CO_2, and iodine (Berthelot, *A. Ch.* [4] 3, 211). 4. *Mercuric chloride* in the cold forms C_2H_4ClI. At 100° it forms $C_2H_4Cl_2$ (Maumené, *C. R.* 68, 727).—5. *Silver picrate* forms the compound $CH_2I.CH_2.O.C_6H_2(NO_2)_3$ [70°], crystallising in light yellow prisms, insol. water, sl. sol. cold alcohol and ether, v. sol. chloroform (Andrews, *B.* 13, 244).

ETHYLENE IODO-CHLORIDE $CH_2I.CH_2Cl$. *Chloro-iodo-ethane.* (140° cor.) (Thorpe, *C. J.* 37, 189). S.G. $\frac{0}{0}$ 2·1644; $\frac{15·3}{0}$ 2·1336 (T.). Obtained by agitating an aqueous solution of ICl containing a trace of free iodine with ethylene iodide or ethylene (Maxwell Simpson, *Pr.* 11, 590; 12, 278). Colourless oil with sweet taste, sl. sol. water. Moist Ag_2O at 180° forms glycol. Silver at 160° gives AgI, ethylene, and ethylene chloride (Friedel a. Silva, *Bl.* [2] 17, 242).

ETHYLENE LACTIC ACID *v.* HYDRACRYLIC ACID.

ETHYLENE MALONIC ACID *v.* TRI-METHYLENE DICARBOXYLIC ACID.

ETHYLENE MERCAPTAN $C_2H_4(SH)_2$. (146°). S.G. $\frac{23·5}{}$ 1·123. Formed by the action of alcoholic KHS on ethylene chloride or bromide (Löwig a. Weidmann, *P.* 49, 132; *A.* 36, 322; Kekulé, *K.* 1, 655). Liquid, v. sol. alcohol. Sol. aqueous alkalis. Oxidised by HNO_3 to the acid $C_2H_4(SO_3H)_2$. When HCl is passed through a mixture of ethylene mercaptan with chloral there is formed the compound $C_2H_4(S.CH(OH).CCl_3)_2$. [116°], which crystallises from ether in shining plates (Fasbender, *B.* 21, 1476). In general ethylene mercaptan combines with aldehydes, with evolution of heat, forming additive products, which are decomposed by water into their constituents. When HCl is passed into equimolecular mixtures of ethylene mercaptan and an aldehyde, condensation takes place, an alkylated ethylene mercaptan being formed.

Salts.—$C_2H_4S_2Pb$: light-yellow. $C_2H_4S_2Cu$: green.

Di-methyl derivative $C_2H_4(SMe)_2$. (183°). From ethylene bromide, and NaSMe (Ewerlöf, *B.* 4, 716).

Di-ethyl derivative $C_2H_4(SEt)_2$. (c. 211°).

Di-isoamyl derivative $C_2H_4(SC_5H_{11})_2$. (215°-255°). Gives on oxidation $C_2H_4(SO.C_5H_{11})_2$ [145°-150°].

Benzylidene derivative $C_2H_4S_2CH.C_6H_5$. [29°]. From benzoic aldehyde, ethylene mercaptan, and HCl. Insol. water, sol. alcohol and ether (Fasbender, *B.* 20, 460; 21, 1476).

p-Methoxy-benzylidene derivative $C_2H_4S_2CH.C_6H_4.OMe$. [65°]. From anisic aldehyde and ethylene mercaptan (F.).

Acetylene derivative $C_2H_4S_2.CH.CH.S_2C_2H_4$. [133°]. From glyoxal and ethylene mercaptan.

Ethylidene derivative $C_2H_4S_2CHMe$. (173°). Oxidises to a disulphone [198°].

Propylidene derivative $C_2H_4S_2CHEt$. (192°). Gives a disulphone [124°].

Iso-propylidene derivative $C_2H_4S_2CMe_2$. (171°). From acetone, ethylene mercaptan, and HCl (F.). Potassium permanganate gives by oxidation $C_2H_4(SO_2)_2CMe_2$ [232°].

Di-phenyl-methylene derivative $C_2H_4S_2CPh_2$ [106°].

ω-Chloro-ethyl-ethyl derivative $EtS.C_2H_4.S.CH_2.CH_2Cl$. From ethylated ethylene mercaptan, $Et.S.C_2H_4.SH$ by treatment with KOH and glycolic chlorhydrin, the product, $Et.S.C_2H_4.S.C_2H_4.OH$ being then mixed with PCl_3 in the cold (Demult a. V. Meyer, *A.* 210, 312). Needles. Decomposed by distillation into EtCl and di-ethylene-di-sulphide.

ETHYLENE - METHYL- *v.* Methyl-ethylene-.

ETHYLENE-NAPHTHALENE *v.* Acenaphthene.

ETHYLENE-NAPHTHOIC ACID $C_2H_4:C_{10}H_5.CO_2H$. [217°]. Colourless needles. Obtained by boiling its amide with alcoholic KOH (Gattermann, *A.* 214, 58).

Amide $C_2H_4:C_{10}H_5.CONH_2$. [198°]. Formed by the action of $ClCONH_2$ on acenaphthene in presence of Al_2Cl_6. Colourless plates.

ETHYLENE-NAPHTHYL BENZYL KETONE $C_2H_4:C_{10}H_5.CO.CH_2.C_6H_5$. [114°]. From acenaphthene, phenyl-acetic chloride and Al_2Cl_6 (Päpcke, *B.* 21, 1312). Long plates (from alcohol). V. sol. hot alcohol.

ETHYLENE - NAPHTHYL DI - PHENYL - ETHYL KETONE $C_2H_4:C_{10}H_5.CO.CHPh.CH_2Ph$. [104°]. From the preceding by treatment with benzyl chloride and NaOEt (Papcke, *B.* 21, 1313).

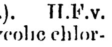
ETHYLENE NITRITE $C_2H_4(O.NO)_2$. (96°). S.G. $\frac{0}{0}$ 1·2156. Prepared by distilling glyceryl trinitrite with glycol (Bertoni, *G.* 15, 351). Yellow oil, sol. alcohol, ether, and chloroform. Gives a violet colouration with conc. H_2SO_4. When distilled with methyl alcohol it yields methyl nitrite and glycol. Gradually converted into oxalic acid on exposure to air. When inspired it produces vertigo and paralysis of the respiratory system.

Isomeride of ethylene nitrite $C_2H_4(NO_2)_2$? [38°]. Formed by passing dry ethylene through liquid nitric peroxide, or by passing ethylene into dry ether, to which N_2O_4 is at the same time added by drops (Semenoff, *Zeit. Ch. Pharm.* 1864, 129). White four-sided prisms or tables, insol. water, v. sol. alcohol and ether. When a gaseous mixture of ethylene and N_2O_4 is heated to 65° there is formed, besides the compound [38°], a pungent, volatile, and poisonous, heavy oil, which is perhaps identical with the oil described by Bertoni as the true ethylene nitrite.

ETHYLENE NITRITE-NITRATE $C_2H_4(NO_2)(NO_3)$? S.G. 1·472. A pungent oil formed when ethylene is passed through a cooled mixture of HNO_3 and H_2SO_4 or into fuming HNO_3 (Kekulé, *Z.* [2] 5, 601). Decomposed by distillation with steam, yielding NO, nitrous fumes, oxalic, glycollic, and glyoxylic acids. Bases produce the same bodies. Sodium-amalgam reduces it in alkaline solution to glycol, giving off NH_3.

ETHYLENE-DI-OXAMIC ETHER $C_2H_4(NH.CO.CO_2Et)_2$. From oxalic ether and ethylene-diamine, remaining in solution when the following body is ppd. (Hofmann, *B.* 5, 247). Scales, sol. water and alcohol.

ETHYLENE-OXAMIDE $C_2O_2N_2H_2C_2H_4$. From oxalic ether and ethylene-diamine (Hofmann, *B* 5, 247). Amorphous, insol. water and alcohol.

ETHYLENE OXIDE C_2H_4O *i.e.*  $\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>O$.

Mol. w. 44. (13·5°). S.G. $\frac{0}{0}$ ·897. V.D. 1·42 (calc. 1·53). H.F.p. 18,090 (*Th.*). H.F.v. 17,220 (*Th.*). Formed by warming glycolic chlorhydrin (chloro-ethyl-alcohol) $CH_2Cl.CH_2OH$ with potash and collecting in a receiver at −18° (Wurtz, *C. R.* 48, 101; 49, 898; 50, 1195; 53, 378; 54, 277; *A* 110, 125; 114, 51; 116, 249; *A. Ch.* [3] 55, 418, 427; 69, 317; *C. J.* 15, 387). Formed also by treating $C_2H_4Br_2$ or $C_2H_4I_2$ with Ag_2O at high temperatures (Greene, *C. R.* 85, 624). From $CH_2(OAc).CH_2Cl$ and KOH (Demole, *A.* 173, 125). Mobile colourless liquid. Miscible with water and alcohol. Does not unite with $NaHSO_3$, or with NH_3. Cannot be dried by $CaCl_2$. Behaves as a strong base, uniting directly with HCl, HOAc, &c. Ppts. from magnesium, aluminium, ferric, and cupric salts, the hydrates of the metals, *e.g.*

$$2C_2H_4O + MgCl_2 + 2H_2O$$
$$= Mg(OH)_2 + 2C_2H_4Cl.OH.$$

Reactions.—1. *Sodium amalgam* reduces it to alcohol, glycol and polyethylenic glycols being also formed.—2. Unites with HCl forming $CH_2Cl.CH_2OH$. The union $C_2H_4O + HCl$, both being gaseous, evolves 3,600 units of heat (Berthelot, *C. R.* 93, 185).—3. Unites with HOAc, giving $CH_2(OH).CH_2(OAc)$.—4. Ac_2O gives $CH_2(OAc).CH_2(OAc)$ and the polyethylenic diacetates $(C_2H_4O)_nAc_2O$.—5. When heated with *water* in sealed tubes it forms glycol and the polyethylenic glycols.—6. *Bromine* (1 mol.) mixed with ethylene oxide (2 mols.), and cooled by a freezing mixture, forms $(C_2H_4O)_2Br_2$, crystallising in prisms [65°], insol. water, sol. alcohol.—7. *Ammonia* forms oxy-ethyl-amine and compounds of the formula $C_2H_4(OH)(OC_2H_4)_nNH_2$.—8. Heated with $NaHSO_3$ in a sealed tube at 100° it gives $CH_2(OH).CH_2.SO_3Na$ (Erlenmeyer, *Z.* [2] 4, 342).—9. Resinifies aldehyde when heated with it in a sealed tube.—10. PCl_5 gives ethylene chloride.—11. *Phosphonium iodide* gives PH_3 and ethylene iodide (De Girard. *C. R.* 101, 478).

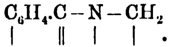
Di-ethylene dioxide $C_2H_4\langle{}^{O}_{O}\rangle C_2H_4$. [9°]. (102°). S.G. $\frac{0}{}$ 1·048. V.D. 3·10 (calc. 3·05). Formed by treating the compound $(C_2H_4O)_2Br_2$ (*v. supra*) with H_2S or, better, with mercury in the cold (Wurtz). Liquid with faint odour. Sol. alcohol and ether, not attacked by ammonia.

Polymeride of ethylene oxide $(C_2H_4O)_x$. [56°]. Formed by leaving ethylene oxide for some months after addition of a very small fragment of fused potash or $ZnCl_2$ (Wurtz, *Bl.* [2] 29, 530; *C. R.* 86, 1176). A trace of HCl will not effect the change. It is a nodular crystalline mass; v. sol. water, insol. ether. It does not reduce Fehling's solution.

Chloro-ethylene oxide C_2H_3ClO. (70°–80°). From CHCl:CHI (1 vol.) and water (15 vols) at 210° (Sabanejeff, *A.* 216, 268).

Bromo-ethylene oxide C_2H_3BrO. (c. 91°). From $CHBr_2.CH_2OH$ and KOH in MeOH (Demole, *B.* 9, 51).

ETHYLENE-PHENANTHRAQUINOXALINE $C_{16}H_{12}N_2$ *i.e.*



$$\begin{array}{cccccc} C_6H_4. & C & - & N & - & CH_2 \\ | & \| & & | & & | \\ C_6H_4. & C & - & N & - & CH_2 \end{array}.$$

Ethylene-di-phenylene-quinoxaline. [181°]. Formed by mixing phenanthraquinone and ethylene-diamine in warm acetic acid solution (Mason, *B.* 19, 112). Distils undecomposed at a high temperature. Yellowish needles. V. sol. ether, benzene, and acetic acid, sl. sol. cold alcohol, insol. water.

ETHYLENE-DI-PHENYL-DIAMINE *v.* DI-PHENYL-ETHYLENE DIAMINE.

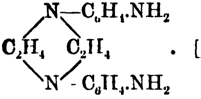
ETHYLENE-DI-PHENYL-DI-CARBAMATE *v. Ethylene ether* of PHENYL-CARBAMIC ACID.

ETHYLENE-PHENYLENE-DIAMINE *v.* PHENYLENE-ETHYLENE-DIAMINE.

Ethylene-di-phenylene-*m*-tetramine $[3:1]C_6H_4(NH_2).NH.C_2H_4.NH.C_6H_4(NH_2)[1:3]$. *Di-m-amido-di-phenyl-ethylene-diamine.* [107°]. Formed by reduction of di-*m*-nitro-di-phenyl-ethylene-diamine. Silvery needles or tables (from hot water). Nearly insol. cold water.

Salts. With nitrous acid they give a brown colouration.—$B''H_4Cl_4$: soluble colourless plates. The picrate forms long brown sparingly soluble needles. The tin-double-chloride is sl. sol. cold water (Gattermann a. Hager, *B.* 17, 779).

Di-ethylene-di-phenylene-tetramine



$$\begin{array}{ccc} & N - C_6H_4.NH_2 & \\ \diagup & & \diagdown \\ C_2H_4 & & C_2H_4 \\ \diagdown & & \diagup \\ & N - C_6H_4.NH_2 & \end{array}.$$

[221°]. Prepared by reduction of dinitroso-diphenyl-diethylene-diamine (Morley, *B.* 12, 1796). Silvery leaflets. Sl. sol. alcohol, ether, and C_6H_6. Violet colouration with Fe_2Cl_6.

ETHYLENE-DI-PHENYLENE-NITRAMINE *v.* DI-NITRO-DI-PHENYL-ETHYLENE-DIAMINE.

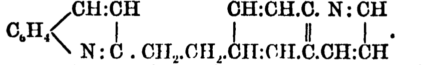
ETHYLENE-DI-PHENYL-DI-SULPHONE *v.* DI-PHENYL-ETHYLENE-DI-SULPHONE.

ETHYLENE-DIPHTHALIMIDE $(C_6H_4C_2O_2N)_2C_2H_4$. [232°]. From potassium phthalimide (10 g.) and ethylene bromide (12 g.) at 200°, the chief product of the reaction being $C_6H_4.C_2O_2.N.C_2H_4Br$ [83°] (Gabriel, *B.* 20, 2224). Long lustrous needles (from HOAc). Fuming HCl at 200° splits it up into ethylene-diamine and phthalic acid.

ETHYLENE PROPYLIDENE DISULPHONE *v.* ETHYLENE MERCAPTAN.

ETHYLENE DIPROPYL DISULPHONE $C_2H_4(SO_2Pr)_2$. [155°]. From sodium ethane disulphinate and propyl bromide (Otto, *J. pr.* [2] 36, 446). Iridescent prisms.

ETHYLENE-DI-QUINOLINE $C_{20}H_{16}N_2$ *i.e.*



$$C_6H_4\left\langle\begin{array}{l} CH{:}CH \qquad\qquad\qquad CH{:}CH.C.\ N{:}CH \\ \qquad\ | \qquad\qquad\qquad\quad | \qquad\qquad \| \qquad\ | \\ N{:}C\,.\,CH_2.CH_2.CH{:}CH.C.CH{:}CH \end{array}\right..$$

[106·5°]. Prepared by the action of HI and amorphous phosphorus on acetylene-di-quinoline [147°], itself prepared from *p*-amido-(*Py.* 3)-styryl-quinoline by treatment with *o*-nitrophenol, glycerin, and H_2SO_4 (Balach, *B.* 22, 289). Glistening prisms (from hot water).

ETHYLENE SELENOCYANIDE $C_2H_4(SeCy)_2$. [128°]. From potassium selenocyanide and ethylene bromide (Proskauer, *B.* 7, 1281). White needles (from alcohol), insol. cold water and ether, sl. sol. hot water and cold alcohol. Boiling nitric acid oxidises it to $C_2H_4(SeO_3H)_2$ which is deliquescent.

ETHYLENE SULPHIDE C_2H_4S. This perhaps constitutes the amorphous pp. obtained when ethylene bromide is mixed with alcoholic KHS. It is nearly insol. alcohol, ether, and CS_2. At 160° it changes to di-ethylene-disulphide (Löwig a. Weidmann, *P.* 49, 123). When ethylene sulphide is heated with MeI in a sealed tube at 65° it forms a sulphine iodide which resembles SMe_3I rather than $(C_2H_4)_2S_2MeI$ in crystalline form and solubility (Masson, *C. J.* 49, 249).

Di-ethylene di-sulphide $C_2H_4\langle{}^{S}_{S}\rangle C_2H_4$. Mol. w. 120. [112°]. (200°). V.D. 4·28 (calc. 4·16). Formed by heating the preceding at 160° (Crafts, *A.* 124, 110). Obtained also by heating ethylene tri-thiocarbonate $C_2H_4CS_3$ or ethylene mercaptide of mercury $C_2H_4S_2Hg$ with $C_2H_4Br_2$ at 150° (Husemann, *A.* 126, 280).

Properties.—Monoclinic prisms (from CS_2), sol. alcohol and ether. Readily sublimed.

Reactions.—1. *Bromine* forms $(C_2H_4)_2S_2Br_4$, a yellow amorphous pp. [96°].—2. *Iodine* gives $C_4H_8S_2I_2$ [133°]: black monoclinic needles.—3. Fuming HNO_3 forms $(C_2H_4)_2(SO)_2$ below 100°, but above 150° it gives $(C_2H_4)_2(SO_2)_2$ (Crafts, *A.* 125, 123).

Combinations. $C_4H_8S_2HgCl_2$: crystalline pp. got by mixing alcoholic solutions of $C_4H_8S_2$ and $HgCl_2$.—$C_4H_8S_2HgI_2$: minute trimetric tables.—$C_4H_8S_2PtCl_4$: amorphous orange powder.—$C_4H_8S_2 2AuCl_3$: vermillion pp.—$(C_4H_8S_2)_3 4AgNO_3$: small monoclinic crystals; decomposing at 140°.

Methylo-iodide $(C_2H_4)_2S_2MeI$. From di-ethylene di-sulphide and MeI at 70° (Masson, *C. J.* 49, 238). Opaque white needles, v. sol. hot, sl. sol. cold, water, v. sol. alcohol, insol. ether. Sublimes above 100°, some $(C_2H_4)_2S_2$ being regenerated.

Methylo-tri-iodide $(C_2H_4)_2S_2MeI_3$. [89°] (Masson); [93°] (Mansfeld, *B.* 19, 2658). From the methyl-iodide and iodine. Thin lustrous garnet-red plates, v. sol. hot, sl. sol. cold, alcohol, insol. ether.

Di-methylo-iodide $(C_2H_4)_2S_2Me_2I_2$. [208°].

Methylo-nitrate $(C_2H_4)_2S_2MeNO_3$. [172°]. From the iodide and $AgNO_3$ (Masson). Pearly plates or rhombic crystals, v. e. sol. water,

m. soluble in hot alcohol, insoluble in ether.—$(C_2H_4)_2S_2MeNO_3AgNO_3$: colourless barb-like crystals, v. e. sol. water, m. sol. alcohol, insol. ether; blackens in sunlight; detonates slightly when heated.

Methylo-sulphate $\{(C_2H_4)_2S_2\}_2Me_2SO_47aq.$ [127°]. From the iodide and Ag_2SO_4. Large deliquescent prisms (from water) or small needles (from alcohol). Decomposed by fusion.

Methylo-chloride $(C_2H_4)_2S_2MeCl$. [225°] (Mansfeld, *B.* 19, 2658). From the sulphate and $BaCl_2$. Needles or tables; v. sol. water, sl. sol. alcohol, insol. ether (Masson, *C. J.* 49, 242). $(C_4H_8S_2MeCl)_2PtCl_4$: orange crystalline powder, got by adding $PtCl_4$ to a cold solution of the chloride.—$C_{10}H_{21}S_4Pt_2Cl_9$: formed by digesting the preceding compound with boiling water.—$(C_4H_8S_2MeCl)_43PtCl_4$: formed, together with the following, by adding $PtCl_4$ to a hot solution of the methylo-chloride. Orange amorphous pp., insol. water, alcohol, ether, and dilute acids, sl. sol. hot conc. HClAq, sol. conc. NH_3Aq. Cold H_2S does not affect it, but it is decomposed by H_2S at 100°.—$C_4H_8S_2MeClPtCl_4$: obtained by fractionally ppg. a solution of the methylo-chloride with $PtCl_4$. Orange amorphous pp.—$C_4H_8S_2MeClAuCl_3$: light-yellow amorphous powder; decomposed by heating with water.—$C_4H_8S_2ClHgCl_2$: needles and thin plates, obtained by mixing aqueous solutions of its components.

Methylo-hydroxide $(C_2H_4)_2S_2MeOH$. Formed in solution by treating a very dilute solution of the iodide with moist Ag_2O in the cold. It ppts. solutions of metallic salts and absorbs CO_2 from the air. On boiling there is formed a white flocculent pp. and an oil $C_{12}H_{24}S_5$; S.G. $^{16}_{15\cdot5}$ 1·044. This oil has a disagreeable odour, is insol. water, sol. alcohol and ether: volatile with steam. It combines with MeI. This oil is also formed when an aqueous solution of the chloride, iodide, sulphate, or nitrate is heated with potash or baryta-water. Mansfeld considers the oil to be $C_5H_{10}S_2$, and finds it can take up (2 mols. of) bromine.

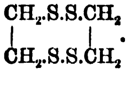
Methylo-picrate $(C_2H_4)_2S_2MeO.C_6H_2(NO_2)_3$. [193°]. Golden needles (Mansfeld).

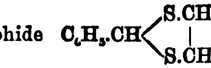
Benzylo-bromide $(C_2H_4)_2S_2C_7H_7Br$. [146°]. From $(C_2H_4)_2S_2$ and benzyl bromide at 150° (Mansfeld, *B.* 19, 2666). Trimetric crystals (from water). Sl. sol. water and alcohol. Potash (1 mol.) converts it on warming into oily $C_{11}H_{14}S_2$, which is slightly volatile with steam.

Benzylo-chloride $(C_2H_4)_2S_2C_7H_7Cl$. [143°]. From the bromide and AgCl. Colourless silky needles.

Benzylo-iodide $(C_2H_4)_2S_2C_7H_7I$. From di-ethylene di-sulphide and benzyl iodide at 100°. Pale-yellow needles, sl. sol. water, m. sol. alcohol, insol. ether.

Benzylo-picrate $(C_2H_4)_2S_2C_7H_7OC_6H_2(NO_2)_3$. [112°]. Golden needles.

Di-ethylene-tetra-sulphide  $\begin{matrix}CH_2.S.S.CH_2\\ | \qquad\quad | \\ CH_2.S.S.CH_2\end{matrix}$. [152°] ?

Formation.—1. By the action of bromine upon a chloroform solution of ethylene mercaptan $C_2H_4(SH)_2$ or of benzylidene-ethylene-di-sulphide  $C_6H_5.CH\begin{smallmatrix}\diagup S.CH_2\\ \quad | \\ \diagdown S.CH_2\end{smallmatrix}$.—2. By treating ethylene mercaptan with conc. H_2SO_4 or with SO_2Cl_2.—3. By the action of hydroxylamine hydrochloride on an alkaline solution of ethylene mercaptan.

Properties.—Amorphous powder. Softens at 141°, melts at 152°. Almost insol. all solvents. Sol. phenol. Not volatile (Fasbender, *B.* 20, 462; 21, 1471). It forms a perbromide $C_4H_8S_4Br_8$: unstable brownish-red crystals. HNO_3 gives ethylene disulphonic acid.

DI-ETHYLENE SULPHOBROMIDE $(C_2H_4)_2SBr_2$. Formed by heating ethyl sulphide with ethylene bromide and water (1 vol.) at 130° (Dehn, *A. Suppl.* 4, 83; *cf.* Masson, *C. J.* 49, 253). It is said to give $(C_2H_4)_2SCl_2PtCl_4$.

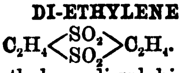
ETHYLENE SULPHOCHLORIDE. A name given by Guthrie to various oils got by the action of the chlorides of sulphur on ethylene (*q. v.*).

ETHYLENE DI-SULPHOCYANIDE $C_2H_4(SCN)_2$. [90°]. S.G. $^{\underline{15}}$ 1·28.

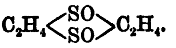
Formation.—1. By heating an alcoholic solution of ethylene chloride or bromide with an equivalent quantity of potassium sulphocyanide at 100° (Sonnenschein, *J. pr.* 65, 257; Buff, *A.* 96, 302; 100, 219; Glutz, *A.* 153, 313).—2. From KSCN, $C_2H_4Cl.SCN$, and alcohol (James, *C. J.* 43, 40).

Properties.—Stellate groups of small needles (from water) or large trimetric plates (from alcohol). Burning taste; blisters the skin. Its vapour excites sneezing. HNO_3 oxidises it to ethane disulphonic acid $C_2H_4(SO_3H)_2$. Boiling aqueous KOH or baryta saponify it, forming sulphocyanides.

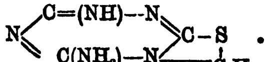
Reactions.—1. *Tin* and *hydric chloride* give $CyS.C_2H_4.SH_2Cl$, which crystallises from alcohol in scales, and forms a tin double salt $(C_3H_6NS_2Cl)_2SnCl_2$ (Glutz). The corresponding compounds, $C_3H_6NS_2I$ which melts above [100°], $C_3H_6N.S_2NO_3\frac{1}{2}aq$, and $C_3H_6NS_2SCy$ are crystalline.—2. PEt_3 forms PEt_3S and $C_2H_4(PEt_3CN)_2$ (Hofmann, *A. Suppl.* 1, 55).—3. A warm conc. solution of Na_2SO_3 forms crystals of $CH_4S_3NO_{10}Na_3$ (?), while the mother-liquor contains $C_4H_{10}S_9O_{12}Na_4$ (Glutz).

DI-ETHYLENE DI-SULPHONE  $C_2H_4<\begin{smallmatrix}SO_2\\ SO_2\end{smallmatrix}>C_2H_4$. Formed by heating di-ethylene di-sulphide with fuming HNO_3 for 30 minutes at 150° (Crafts, *A.* 125, 124). Formed also by the action of di-bromo-ethane on sodium ethane disulphinate (Otto, *J. pr.* [2] 36, 446). Prisms, insol. ordinary solvents, m. sol. hot conc. HNO_3.

ETHYLENE DISULPHONIC ACID *v.* ETHANE DISULPHONIC ACID.

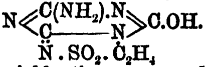
DI-ETHYLENE DISULPHOXIDE  $C_2H_4<\begin{smallmatrix}SO\\ SO\end{smallmatrix}>C_2H_4$. From di-ethylene di-sulphide and fuming HNO_3 (Crafts, *A.* 124, 113; 125, 123). Formed also by treating $(C_2H_4)_2S_2Br_4$ with water (Husemann, *A.* 126, 290). Rhombohedra or long white prisms; decomposed by heat without melting. V. sol. water, sl. sol. alcohol and ether. Chlorine passed into its solution gives a crystalline pp. of $C_4H_8Cl_2S_2O_2$.

ETHYLENE THIO-AMMELINE $C_5H_7N_5S$ *i.e.*



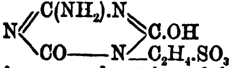
$N\left<\begin{matrix}C{=}(NH){-}N\\C(NH_2){-}N\end{matrix}\right>C{-}S \,|\, C_2H_4$. Formed by heating ethylene bromide, alcohol, and thio-ammeline to 120° (Rathke, *B.* 21, 874).

Reactions.—1. By passing *chlorine* through a solution of the hydrochloride in water an anhydride of 'tauroammeline' is formed. This anhydride forms plates, insol. water, sol. alkalis; it may be written



$N\left<\begin{matrix}C(NH_2).N\\C{-}N\end{matrix}\right>C.OH$; $\dot{N}.SO_2.\dot{C}_2H_4$.

2. Oxidation with HNO_3 yields the compound $C_{10}H_{15}N_9S_2O_8$. This compound has been called 'tauro-di-ammeline,' and crystallises from water in transparent prisms. It does not melt below 290°. It reddens blue litmus, liberates CO_2 from carbonates, and forms very soluble salts of K, Na, Ca, and Ba. Its ammoniacal solution gives with $AgNO_3$ a pulverulent pp. not affected by light. On boiling with baryta it changes to 'tauro-ammelide'



$N\left<\begin{matrix}C(NH_2).N\\CO{-}N{-}C_2H_4.SO_3H\end{matrix}\right>C.OH$ [c. 267°], which forms moderately soluble crystals, and gives with ammoniacal copper solution a pp. of flat amethyst-coloured needles.

ETHYLENE DI-THIO-CARBONATE $C_2H_4COS_2$. [31°]. From ethylene-tri-thio-carbonate by treatment with moderately dilute nitric acid (Husemann, *A.* 126, 269). Long thin rectangular tables (from alcohol). May be distilled in a current of hydrogen; insol. water, v. sol. alcohol, ether, chloroform, and benzene.

Ethylene tri-thio-carbonate $C_2H_4CS_3$. [37°]. S.G. 1·477. From Na_2CS_3 and an alcoholic solution of ethylene bromide (Husemann, *A.* 123, 83). Large yellow crystals (from ether-alcohol), with alliaceous odour, sl. sol. alcohol, v. sol. benzene, CS_2, and chloroform. Converted by ammonia into ethylene mercaptan and ammonium sulphocyanide. KHS gives K_2CS_3 and ethylene mercaptan. Fuming HNO_3 gives $C_2H_4(SO_3H)_2$.

ETHYLENE THIO-UREA $C_3H_6N_2S$ *i.e.* $CS\left<\begin{matrix}NH\\NH\end{matrix}\right>C_2H_4$. [194°]. An alcoholic solution of ethylene-diamine mixed with CS_2 deposits in a short time amorphous $C_3H_8N_2S_2$ (or $CS\left<\begin{matrix}S.NH_3\\NH{-}\end{matrix}\right>C_2H_4$?), insol. alcohol and ether, which, when boiled with water, gives off H_2S, leaving ethylene thio-urea (Hofmann, *B.* 5, 240). Prisms (from water). Sl. sol. ether, v. sol. alcohol. Tastes bitter. Not altered by digestion at high temperatures with CS_2 and PbO.

Combinations.—$(C_3H_6N_2S)_2 3HgCl_2$.—$(C_3H_6N_2S)_2PtCl_4$.—$(C_3H_6N_2S)_2H_2PtCl_6$: obtained by heating ethylene thio-urea with conc. H_2SO_4, diluting with water, and adding platinic chloride.

Ethylene-di-thio-di-urea $C_4H_{10}N_4S_2$ *i.e.* $C_2H_4(NH.CS.NH_2)_2$. The hydrobromide $B''H_2Br_2$ is formed by boiling thio-urea with $C_2H_4Br_2$ in alcohol (Andreasch, *M.* 4, 142). This salt forms long broad prisms, sol. cold water. HCl and $KClO_3$ oxidise it to urea and $C_2H_4(SO_3H)_2$. The hydrochloride $B''H_2Cl_2$ forms geodes of slender needles.

ETHYLENE-TOLYL- *v.* TOLYL-ETHYLENE-; and *infra.*

ETHYLENE - DI - *p* - TOLYLENE - TETRA - AMINE

$C_6H_3(CH_3)(NH_2).NH.C_2H_4.NH.C_6H_3(CH_3)(NH_2)$. *Di-m-amido-di-p-tolyl-ethylene-diamine.* [159° uncor.]. Formed by reduction of di-*m*-nitro-di-*p*-tolyl-ethylene-diamine (Gattermann a. Hager, *B.* 17, 779). Long colourless needles. Sol. alcohol, sl. sol. water.

ETHYLENE-DI-TOLYLENE-NITRAMINE *v.* DI-NITRO-DI-TOLYL-ETHYLENE-DIAMINE.

ETHYLENE-UREA $C_3H_6N_2O$ *i.e.* $C_2H_4\left<\begin{matrix}NH\\NH\end{matrix}\right>CO$. [131°]. Formed by heating ethylene-diamine with ethyl carbonate at 180° (Fischer a. Koch, *A.* 232, 227). Needles v. sol. water and hot alcohol, sl. sol. ether. Gives with HNO_3 a di-nitro-derivative without any evolution of gas (Franchimont, *R. T. C.* 6, 219).

Ethylene-di-urea $C_4H_{10}N_4O_2$ *i.e.* $C_2H_4(NH.CO.NH_2)_2$. [192°]. From silver cyanate and the hydrochloride of ethylene-diamine (Volhard, *Pr.* 11, 268). Prisms, sol. water and alcohol. Dissolves in HClAq, but separates unaltered on evaporation. Boiling conc. KOHAq gives ethylene-diamine, CO_2, and ammonia. With a solution of mercuric nitrate it gives a flocculent pp. It is immediately attacked by pure HNO_3, giving off CO_2 and N_2O in equal volumes (Franchimont, *R. T. C.* 6, 219).—$B'_2H_2PtCl_6$: orange-red prisms.—$B'HAuCl_4$: golden scales.

ETHYLENE-DI-URETHANE *v.* ETHYLENE DICARBAMIC ETHER.

ETHYL-ETHANE CARBOXYLIC ACID *v.* BUTANE-CARBOXYLIC ACID.

ETHYL-ETHENYL CARBOXYLIC ACID *v.* BUTANE TRI-CARBOXYLIC ACID.

ETHYL ETHER *v.* ETHER.

ETHYL-ETHYLENE *v.* BUTYLENE.

TETRA-ETHYL FERRO-CYANIDE Et_4FeCy_6. [214°]. Formed by the action of silver ferrocyanide on ethyl iodide (Freund, *B.* 21, 935). Rhombic crystals (from chloroform). V. sol. water, alcohol, chloroform, insol. ether, petroleum ether, and CS_2. Is decomposed by conc. H_2SO_4 with evolution of CO_2. $HgCl_2$ gives a white pp.

ETHYL - FLAVANILINE $C_{16}H_{13}N_2(C_2H_5)$. Orange colouring matter.—B'HI: long red needles. Formed by heating flavaniline with ethyl-iodide (Fischer a. Rudolph, *B.* 15, 1502).

ETHYL FLUORIDE C_2H_5F. (−48°). V.D. 1·70. S. (gas) 1·98. Produced by distilling a mixture of fluor-spar, alcohol, and H_2SO_4 or by warming $KEtSO_4$ with KHF_2 (Reinsch, *J. pr.* 19, 514; Fremy, *A.* 92, 247). Prepared by passing EtI over AgF heated to 40° in leaden tubes, and collected over mercury in dry glass vessels (Moissan, *C. R.* 107, 260). Gas, v. sol. EtI and EtBr. Under 8 atmospheres' pressure it liquefies at 19°. Burns with a blue flame. Heated to dull redness in a glass bulb it gives a mixture of hydrocarbons together with traces of fluoride of silicon. Subjected to a weak induction spark its volume increases, and it gives hydrofluoric acid, and small quantities of acetylene and ethylene, but no free carbon. Subjected to a strong induction spark it gives free carbon, also acetylene, ethylene, propylene, &c. Passed through a platinum tube heated to dull redness it yields hydrofluoric acid mixed with hydrocarbons, partly capable of being absorbed by sulphuric acid, and a little free carbon is deposited. Anæsthetic. In large quantities the excitement is followed by death (Moissan, *C. R.* 107, 992).

ETHYL-FORMAMIDE *v. Formyl derivative* of ETHYLAMINE, and also under FORMIC ACID.

***u*-DI-ETHYL-FORMAMIDINE** $HC(NEt_2):NH$. *Form-imid-di-ethyl-amide.* Prepared by allowing an absolute alcoholic solution of the hydrochloride of formimido-ether (1 mol.) and di-ethyl-amine (2 mols.) to stand at the ordinary temperature for several weeks, and then distilling off the alcohol and excess of di-ethyl-amine on the water-bath. When boiled with alcohol it loses NH_3, giving a condensation product $C_{10}H_{21}N_3$. The hydrochloride (B'HCl) forms glistening transparent prisms, very hygroscopic and easily soluble in alcohol [125°].—$B'_2H_2Cl_2PtCl_4$: yellowish-red sparingly soluble prisms [209°] (Pinner, *B.* 17, 179).

***s*-Di-ethyl-formamidine** $HC(NHEt):NEt$. *Form-ethyl-imid-ethyl-amide.* Formed by the action of an alcoholic solution of ethylamine on the hydrochloride of formimido-ether.

Salts.—B'HCl: large deliquescent plates.—$B'_2H_2Cl_2PtCl_4$: thick red prisms [198°] (Pinner, *B.* 16, 1649).

ETHYL FORMANILIDE *v.* FORMIC ACID.

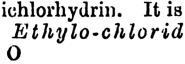
DI-ETHYL-FUMARAMIDE *v. Ethylamide* of FUMARIC ACID.

ETHYL-FURFURINE *v.* FURFURINE.

TRI-ETHYL-GALLIC ACID *v.* GALLIC ACID.

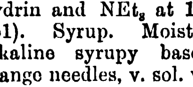
β-ETHYL-GLUTARIC ACID $CH_3.CH_2.CH(CH_2.CO_2H)_2$. [67°]. From malonic acid, propionic aldehyde, and glacial acetic acid at 100° (Komnenos, *A.* 218, 167). The yield is very small (4 p.c. of the malonic acid). Small prisms. V. sol. water, alcohol, ether, or chloroform.

DI-ETHYL-GLYCIDAMINE $C_7H_{15}NO$ *i.e.*



$\overbrace{CH_2.CH}^{O}.CH_2NEt_2$. This constitution is assigned by Reboul (*Bl.* [2] 42, 261) to the substance [160°] formed by the action of di-ethylamine on epichlorhydrin. It is v. sol. water.

Ethylo-chloride $C_9H_{20}NOCl$ *i.e.*



$\overbrace{CH_2.CH}^{O}.CH_2.NEt_3Cl$. Formed from epichlorhydrin and NEt_3 at 100° (Reboul, *Bl.* [2] 42, 261). Syrup. Moist Ag_2O gives a strongly alkaline syrupy base. — $(C_9H_{20}NOCl)_2PtCl_4$: orange needles, v. sol. water, insol. alcohol.

ETHYL-GLYCOCOLL *v.* ETHYL-AMIDO-ACETIC ACID.

ETHYL-DI-GLYCOLAMIC ACID *v.* ETHYL-IMIDO-DI-ACETIC ACID.

ETHYL-GLYCOLLIC ACID *v. Ethyl derivative* of GLYCOLLIC ACID.

ETHYL-GLYOXALINE $C_3H_2(C_2H_5)N_2$. (210°). S.G. ·999. Formed by treating tri-bromo-ethyl-glyoxaline with sodium amalgam (Wyss, *B.* 10, 1373). Prepared by heating glyoxaline with ethyl bromide (Wallach, *B.* 16, 534). Mobile colourless fluid. Miscible with water.

Methylo-iodide B'MeI: [75°]; large prisms.—$(B'MeI)_2CdI_2$: [152°]; plates.

Methylo-chloride B'MeCl; formed by the action of AgCl on the methylo-iodide.—$(B'MeCl)_2PtCl_4$: [195°].—$(B'MeCl)_2ZnCl_2$: transparent soluble crystals [158°].

Ethylo-bromide $C_3H_3EtN_2EtBr$. Formed by heating glyoxaline with EtBr (Wyss, *B.* 10, 1367). Syrup. — $(B'EtCl)_2PtCl_4\frac{1}{2}aq$: pearly plates.

Tri-bromo-ethyl-glyoxaline $C_3Br_3(C_2H_5)N_2$. [62°]. Formed by bromination of ethyl-glyoxaline dissolved in dilute H_2SO_4 (Wallach, *B.* 16, 537). Formed also from silver tri-bromo-glyoxaline and EtI (Wyss, *B.* 10, 1372). Colourless crystals. Insol. cold water.

Para-ethyl-glyoxaline $C_3H_3(C_2H_5)N_2$. [77°] (W.); [80°] (R.); (268°) (R.). Formed by isomeric change from the tertiary ethyl-glyoxaline by passing it through a heated tube (Wallach, *B.* 16, 513). Prepared by the action of propionic aldehyde-ammonia on glyoxal (Radziszewski, *B.* 16, 490). Long prisms. Sol. water, alcohol, ether and benzene, sl. sol. ligroïn. Secondary base.—$B'_2H_2Cl_2PtCl_4$: easily soluble prisms or plates. Heated with propyl bromide it gives an ethyl-propyl-glyoxaline which is probably identical with oxal-propyline (W.).

Para-di-ethyl-glyoxaline $C_3H_2(C_2H_5)_2N_2$. *Oxal-ethyl-propyline.* (220°). S.G. ·9813. Formed by the action of ethyl bromide on ethyl-glyoxaline (glyoxal-propyline) (Radziszewski, *B.* 16, 491). Colourless liquid with narcotic smell. Sol. water, alcohol, and ether. The double-zinc chloride forms crystals melting at [173°].

ETHYL-GLYOXYLIC ACID $C_4H_6O_3$ *i.e.* $Et.CO.CO_2H$. (74°–78°) at 25 mm. S.G. 1·25.

Preparation.—Propionyl cyanide (5 g.) is mixed with HCl (2·5 g. of S.G. 1·23) and kept for 2 hours at 0°. More HCl (2·5 g. of S.G. 1·23) is added, and, after standing, the mixture is diluted with water and heated for 3 hours on the water-bath. The acid is then extracted with ether (L. Claisen a. E. Moritz, *C. J.* 37, 693).

Properties. — Liquid with empyreumatic smell. Miscible with water, alcohol, and ether. Sodium amalgam reduces it to α-oxy-butyric acid [43°].

Salts.—AgA': prisms.—BaA'_2 aq: m. sol. water.

Amide $Et.CO.CO.NH_2$. [117°]. Prepared from propionyl cyanide (2 g.) by mixing with HCl (1 g. of S.G. 1·23) and keeping at 0° for 2 hours. The semi-solid product is left for a week over lime. The amide is then separated from NH_4Cl by sublimation (C. a. M.). It may be crystallised from ether.

Phenyl-hydrazide $Et.C(N_2HPh).CO_2H$ [152°]. Obtained by hydrolysis of the product of the action of diazobenzene chloride on ethyl-aceto-acetic ether (Japp a. Klingemann, *C. J.* 53, 519). Yellow silky needles, decomposed on melting. Reduced by sodium amalgam to benzene-α-hydrazo-butyric acid $Ph.NH.NH.CHEt.CO_2H$.

ETHYL-DIGUANIDE $C_4H_{11}N_5$ *i.e.* $C_2H_6EtN_5$.

Formation.—By heating di-cyan-di-amide (5 pts.) with $CuSO_4$ 5aq (7 pts.), ethylamine (8 pts.), and water (32 pts.) for some hours at 100° there is formed the salt $(C_4H_{11}N_5)_2CuSO_4aq$, whence H_2S removes the copper, and the resulting $(C_4H_{11}N_5)_2H_2SO_4$ is then decomposed by baryta (Emich, *M.* 4, 395).

Preparation.—An alcoholic solution of dicyandiamide is heated with ethylamine hydrochloride in a sealed tube for several hours (Smolka a. Friedreich, *M.* 9, 229).

Properties.—Deliquescent crystalline mass, v. sol. water and alcohol, insol. ether.

Salts.—$B''HCl$: six-sided tables, v. e. sol. water, insol. alcohol and ether.—$B''H_2Cl_2$.—$B''_2H_2SO_4$ $1\frac{1}{2}$aq: small trimetric crystals, *a*:*b*:*c* = 1·04:1:1·36; v. sol. water, insol. alcohol. [180°], when anhydrous.—$B''H_2SO_4$ $1\frac{1}{2}$aq. S. 4 in the cold.—B''_2CuSO_4 aq: minute rose-coloured needles (from cold aqueous solutions).—B''_2CuSO_4: crimson crystalline grains (from hot solutions). S. ·0214 in the cold.—B''_2NiSO_4xaq.—$Cu(C_4H_{10}N_5)_2$: from B''_2CuSO_4 by cautious treatment with aqueous NaOH. Red needles, sl. sol. cold water. $Ni(C_4H_{10}N_5)_2$: obtained by boiling $Ni(OH)_2$ with ethyl-diguanide.—Picrates $B''C_6H_2(NO_2)_3OH$ and $B''2C_6H_2(NO_2)_3OH$ may be crystallised from hot water.

***u*-DI-ETHYL-GUANIDINE** $NH:C(NEt_2)(NH_2)$. From cyanamide and di-ethyl-amine hydrochloride (Erlenmeyer, *B.* 11, 1869). Monoclinic crystals, *a*:*b*:*c* = ·925:1:1·162. $\beta = 74° 35'$—$B'HCl$: monoclinic prisms; *a*:*b*:*c* = ·960:1:·749; $\beta = 63° 59'$.—$B'_2H_2PtCl_6$: orange triclinic tables; *a*:*b*:*c* = ·789:1:·564; $\alpha = 90° 21'$; $\beta = 92° 50'$; $\gamma = 82° 9'$ (Haushofer, *J.* 1881, 330; 1882, 364; *Z. K.* 6, 130; 7, 267).

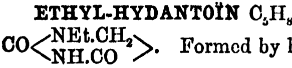
***s*-Tri-ethyl-guanidine** $NEt:C(NHEt)_2$. Formed by boiling an alcoholic solution of di-ethyl-thio-urea with ethylamine and HgO (Hofmann, *B.* 2, 601). Strongly alkaline liquid; absorbs CO_2 from the air.—$B'_2H_2PtCl_6$: crystalline plates, v. sol. water.

ETHYL-*n*-HEPTYL-OXIDE $Et.O.C_7H_{15}$. (166·6°). S.G. $\frac{0}{0}$ ·7949. S.V. 220·8. C.E. (0°–10°) ·001 (Dobriner, *A.* 243, 5; Cross, *A.* 189, 5).

Ethyl heptyl oxide $Et.O.C_7H_{15}$. (177°). S.G. $\frac{16}{}$ ·791. V.D. 5·10 (calc. 4·99). From EtI and the sodium heptylate from castor oil (Wills, *C. J.* 6, 312; Peterson, *A.* 118, 75).

ETHYL-HEXYL-GLYOXALINE $C_{11}H_{20}N_2$. *Oxalethyl-œnanthyline.* (271°). S.G. $\frac{16·5}{}$ ·921. From hexyl-glyoxaline and EtI (Karcz, *M.* 8, 222). Oil.—$B'_2H_2PtCl_6$: yellow soluble plates.

ETHYL HEXYL OXIDE $CH_2Et.CHEt.OEt$. (132°). S.G. $\frac{0}{}$ ·787. From di-chlorinated ether and $ZnEt_2$ (Lieben, *A.* 178, 14). With HI it gives EtI and secondary hexyl iodide.



ETHYL-HYDANTOÏN $C_5H_8N_2O_2$ *i.e.* $CO<\substack{NEt.CH_2\\NH.CO}>$. Formed by heating ethyl-glycocoll with urea at 125° (Heintz, *A.* 133, 65). Tables, melting below 100°. V. e. sol. water and alcohol. May be sublimed.

ETHYL-HYDRAZINE $C_2H_8N_2$ *i.e.* $C_2H_5.NH.NH_2$. (99·5° at 709 mm.). Prepared from *s*-di-ethyl-urea NHEt.CO.NHEt, which is treated with nitrous acid and the resulting nitrosamine NHEt.CO.NEt.NO then reduced by zinc-dust and acetic acid to $NHEt.CO.NEt.NH_2$, whence hot conc. HCl forms NH_2Et, CO_2, and $NHEt.NH_2$. Ethyl-hydrazine hydrochloride being less soluble than ethylamine hydrochloride may be separated from it by crystallisation (Fischer, *A.* 199, 281; *B.* 9, 111).

Properties.—Colourless mobile liquid of faint ammoniacal odour; very hygroscopic; v. sol. water, alcohol, ether, and benzene, sl. sol. conc. KOHAq. It attacks cork and caoutchouc. It fumes in moist air. It gives the carbamine reaction with chloroform and alcoholic potash. Bromine decomposes it, giving off nitrogen. It ppts. metallic oxides from their salts.

Reactions.—1. Reduces Fehling's solution in the cold.—2. Reduces Ag_2O.—3. Reduces HgO forming $HgEt_2$.—4. Reacts with *aldehydes* with considerable evolution of heat, forming ethyl-hydrazides $R.CH:N_2HEt$.—5. Decomposed by *nitrous acid gas.*—6. Its hydrochloride reacts when heated with *potassium cyanate* in aqueous solution with production of ethyl semi-carbazide $NH_2.CO.NH.NHEt$, which forms very soluble leaflets [105°].—7. Its hydrochloride reacts on *phenyl cyanate* in dilute ethereal solution, giving rise to leaflets of phenyl-ethyl-semi-carbazide NHPh.CO.NH.NHEt [111°]; v. sol. alcohol, sl. sol. hot water, decomposed by dilute acids into di-phenyl-urea CO_2, and ethyl-hydrazine.—8. *Phenyl thio carbimide* gives phenyl ethyl thio-semi-carbazide NHPh.CS.NH.NHEt [109°], which crystallises in white leaflets; sl. sol. ether, v. sol. alcohol.—9. *Oxalic ether* gives grouped needles of $C_2O_2(NH.NHEt)_2$ [204°], of which the nitrosamine $C_2O_2(N(NO).N(NO)Et)_2$ [114°] crystallises in prisms and gives Liebermann's reaction.—10. *Picryl chloride* gives $NHEt.NH.C_6H_2(NO_2)_3$ [200°], which forms yellowish-red needles; sl. sol. alcohol, sol. hot benzene, and explode on heating.

Salts. $B''H_2Cl_2$: needles, v. e. sol. water and alcohol, but the solutions on evaporation leave $B''HCl$ as a colourless deliquescent mass. The sulphate forms readily soluble leaflets, the oxalate is a crystalline pp. sol. hot alcohol.

***u*-Di-ethyl-hydrazine** $C_4H_{12}N_2$ *i.e.* $NEt_2.NH_2$. (c. 98°). Formed, together with NH_3 and NEt_2H, by reduction of di-ethyl-nitrosamine $NEt_2.NO$ with zinc and glacial HOAc. The bases are converted into hydrochlorides and, on evaporation, NH_4Cl crystallises first. The filtrate is treated with potassium cyanate and evaporated, when di-ethyl semicarbazide $NH_2.CO.NH.NEt_2$ separates; and this is decomposed by heating with conc. HCl for 12 hours at 100° (Fischer, *A.* 199, 308).

Properties.—Colourless, mobile liquid, of faint ammoniacal odour, sol. water, alcohol, and ether; nearly insol. conc. KOHAq.

Reactions.—1. Reduces hot, but not cold, Fehling's solution, being for the most part converted into diethylamine and nitrogen.—2. *Mercuric oxide* converts it in the cold into tetra-ethyl-tetrazone $Et_2N.N:N.NEt_2$, a non-volatile oil, sol. alcohol, which is decomposed by heat, is volatile with steam, and reduces ammoniacal $AgNO_3$, forming a mirror. Dilute HCl at 80° splits up tetra-ethyl-tetrazone into aldehyde, $NEtH_2$, NEt_2H, and nitrogen. The tetrazone forms a platinochloride $Et_4N_4H_2PtCl_6$, and gives with mercuric chloride a crystalline pp. $Et_4N_4HgCl_2$.—3. *Nitrous acid* forms N_2O and diethylamine (or diethyl nitrosamine).—4. Its hydrochloride is converted by potassium cyanide into *u*-di-ethyl semicarbazide $Et_2N.NH.CO.NH_2$, which forms long prisms [149°], sol. hot water and alcohol, insol. conc. KOHAq. It forms a crystalline nitrosamine $Et_2N.N(NO).CO.NH_2$.

Salts.—The hydrochloride, sulphate,

and nitrate are exceedingly sol. water and alcohol. The picrate and platinochloride $B'_2H_2PtCl_6$ form golden needles.

Ethylo-iodide $NH_2.NEt_3I$. Needles, v. sol. water and hot alcohol, insol. conc. KOHAq and ether. Moist Ag_2O forms a strongly alkaline hydroxide which is decomposed at a higher temperature into water, ethylene, and di-ethyl-hydrazine. It may be reduced by zinc and H_2SO_4 to tri-ethylamine.

ETHYL-HYDRAZINE SULPHONIC ACID $EtN_2H_2.SO_3H$.

Salt.—KA′. Prepared by heating $K_2S_2O_7$ with ethyl-hydrazine at 90°; the mass obtained being warmed with aqueous $KHCO_3$ and evaporated below 70° (Fischer, *A.* 199, 300). Leaflets, sol. water, sl. sol. alcohol. On boiling with strong acids it is decomposed into ethyl-hydrazine and $KHSO_4$. When its aqueous solution is treated with HgO, even in the cold, it yields potassium diazo-ethane sulphonate EtN_2SO_3K in the form of glittering needles or leaflets, sol. alcohol. Diazo-ethane sulphonate explodes violently when heated; it may be reduced by zinc-dust and acetic acid to the parent ethyl-hydrazine sulphonate.

ETHYL-HYDROCARBOSTYRIL *v.* Oxy-ethyl-quinoline dihydride.

ETHYL-HYDROXYLAMINE *v.* Hydroxylamine.

ETHYL HYPOCHLORITE C_2H_5OCl. (36°).

Preparation.—Chlorine is passed through a cold solution of NaOH (1 pt.) in alcohol (1 pt.) mixed with water (9 pts.) as long as the bubbles are absorbed. The ether rises as an oil to the surface and is washed and dried over $CaCl_2$ (Sandmeyer, *B.* 18, 1767; 19, 857).

Properties.—Yellow mobile liquid with very irritating smell. It may be distilled. It is very unstable. On superheating its vapour in a tube it explodes violently. The explosion is also brought about in the cold by contact with precipitated copper. Exposed to diffused daylight it begins to decompose after a few hours' boiling violently; in direct sunshine this decomposition begins in a few minutes and ends with an explosion. It mixes without reaction with ether, chloroform, and benzene. Upon aniline, phenol, &c., it acts like ClOH, oxidising and chlorinating. With HCl, HBr, and HI it at once yields the halogens with liberation of alcohol.

ETHYL HYPOPHOSPHATE $Et_4P_2O_6$. S.G. 15 1·117. From $Ag_4P_2O_6$ and EtI in the cold (Sänger, *A.* 232, 8). Thick colourless liquid. Heated alone it is decomposed into ethyl phosphate and ethyl phosphite. It is saponified by water.—$EtCaHP_2O_6$ 5aq. Needles.

ETHYLIDENE. The divalent radicle $CH_3.CH$. Unlike its isomeride ethylene, it is not known in the free state. By heating ethylidene chloride with sodium at 190° Tollens (*A.* 137, 311) obtained ethylene, acetylene, ethane, and C_2H_3Cl.

ETHYLIDENE DIACETATE *v.* *Di-acetyl derivative* of *Ortho*-aldehyde, vol. i. p. 106.

ETHYLIDENE DI-ACETIC ACID *v.* Methyl-glutaric acid.

ETHYLIDENE-ACETO-ACETIC ETHER is described under Aceto-acetic acid.

ETHYLIDENE-DI-ACETONAMINE *v.* Acetonamine.

ETHYLIDENE-DI-ACETONE-ALCAMINE *v.* Acetone-alcamines.

ETHYLIDENE-DI-ACETONINE *v.* Acetonines.

ETHYLIDENE ALDEHYDATE *v.* Acetal.

ETHYLIDENE-*m*-AMIDO-BENZOIC ACID $C_9H_9NO_2$ *i.e.* $CH_3.CH:N.C_6H_4.CO_2H$. Formed by mixing dilute aqueous solutions of *m*-amidobenzoic acid and aldehyde (Schiff, *A.* 210, 117). Amorphous mass, v. e. sol. alcohol and benzene; melts under boiling water. Long boiling with water decomposes it, CO_2 and ethylidene-aniline being among the products. Conc. HNO_3 containing $K_2Cr_2O_7$ gives a transient violet colour.

ETHYLIDENE-DIAMINE. *Benzoyl derivative* $C_{16}H_{16}N_2O_2$ *i.e.* $CH_3.CH(NHBz)_2$. [204°] (H. a. S.); [188°] (N.). S. (alcohol) 1·24 at 22°.

Formation.—1. From aldehyde-ammonia and BzCl (Limpricht, *A.* 99, 119).—2. By dissolving benzamide in aldehyde to which a few drops of HCl have been added; the reaction being attended with rise of temperature (Nencki, *B.* 7, 158).—3. By gradually adding benzonitrile (2 mols.) to well-cooled conc. H_2SO_4 containing paraldehyde (1 mol.), leaving the liquid to itself for a few hours, and then ppg. the product by water (Hepp. a. Spiess, *B.* 9, 1424).

Properties.—Long needles (from alcohol), v. sol. $CHCl_3$, CS_2, ether, and hot alcohol, nearly insol. water. May be sublimed.

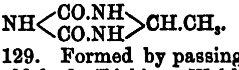
Reactions.—1. With *water* at 130° it gives aldehyde and benzamide.—2. Boiled with dilute (10 p.c.) H_2SO_4 it gives aldehyde, NH_3, and benzoic acid.

Tri-ethylidene-diamine *v.* Aldehyde, *Combination* 4, vol. i. p. 104.

ETHYLIDENE-ANILINE $C_6H_5N:CH.CH_3$ (?). *Aldehyde-anilide.* From ethylidene chloride and aniline at 160° (Schiff, *B.* 3, 415).

Preparation.—A mixture of aniline and aldehyde is made at −18°, then left to itself for some weeks at 15°, and finally heated to 100°. Aniline is removed from the product by dilute HOAc, and the ethylidene-aniline is separated from ethylidene-di-aniline by alcohol, in which it readily dissolves (Schiff, *A.* 140, 127; 210, 114). Red resin.—B'_2HgCl_2.—$B'_4H_2PtCl_6$: orange crystalline pp.

Ethylidene-di-aniline $(C_6H_5.NH)_2CH.CH_3$. Prepared as above. Yellow nodules.—$B'_2H_2Cl_2HgCl_2$.—$B'_2H_2PtCl_6$: orange crystalline pp.

ETHYLIDENE-BIURET $C_4H_7N_3O_2$ *i.e.*  $NH\left\langle\begin{matrix}CO.NH\\CO.NH\end{matrix}\right\rangle CH.CH_3$. *Trigenic acid.* Mol. w. 129. Formed by passing cyanic acid into cold aldehyde (Liebig a. Wöhler, *A.* 59, 296). Small prisms (from water). Sl. sol. water, almost insol. alcohol. Acid to test papers. Decomposed on dry distillation with formation of ammonia, ammonium carbamate, and an oil, which is in all probability a tri-methyl-pyridine, identical with that obtained by Baeyer and Ador (*A.* 155, 294). When heated with MeI and alcohol it yields ammonia and methylamine. With NaOBr it evolves only traces of nitrogen. On oxidation with HNO_3 it is converted into cyanuric acid and carbonic anhydride, a reaction which points to the above formula (Herzig, *M.* 2, 398).—AgA′: pulverulent pp. sol. hot water.

ETHYLIDENE BROMIDE $C_2H_4Br_2$ *i.e.* $CH_3.CHBr_2$. *u-Di-bromo-ethane.* (113°). S.G. $\frac{20\cdot5}{4}$ 2·089 (A.); $\frac{15}{15}$ 2·1029; $\frac{25}{25}$ 2·0854 (Perkin, *C. J.* 45, 523); $\frac{20}{4}$ 2·055 (Weegmann, *Z. P. C.* 2, 218). μ_D 1·5128 (W.). M.M. 9·1.

Formation.—1. By brominating ethyl bromide in sunlight (Staedel, *B.* 11, 1741).—2. From vinyl bromide and HBr (Reboul, *C. R.* 70, 399).

Preparation.—From PCl_3Br_2 and aldehyde in the cold (Paternò a. Pisati, *G.* 1, 596; Anschütz, *A.* 235, 301).

Reactions.—1. *Benzene* and Al_2Cl_6 form ethyl-benzene, *u*-di-phenyl-ethane, and *s*-(*A*)-di-methyl-anthracene di-hydride.—2. Alcoholic KOAc at 130° gives aldehyde, EtOAc, and acetal (Tavildaroff, *A.* 176, 12).—3. Alcoholic KHS has no action (difference from ethylene bromide).—4. *Ammonia* at 130° forms tri-methyl-pyridine (collidine).—5. *Water* and PbO at 130° give aldehyde.—5. $SbCl_5$ forms exclusively $CH_3.CHCl_2$ (Henry, *C. R.* 97, 1491).

ETHYLIDENE BROMO-IODIDE *v.* Bromo-iodo-ethane.

ETHYLIDENE-DI-CARBAMIC ACID. *Ethyl ether* $C_8H_{16}N_2O_4$ *i.e.* $CH_3.CH(NH.CO_2Et)_2$. *Ethylidene-urethane.* [126°]. Formed by the action of aldehyde or acetal on carbamic ether in presence of HCl (Nencki, *B.* 7, 160; Bischoff, *B.* 7, 629). Formed also from aldehyde-ammonia and chloro-formic ether in the cold (Schmid, *J. pr.* [2] 24, 124). Satiny needles; v. sol. ether, alcohol, and hot water. Split up by hot dilute acids into aldehyde and carbamic ether.

Propyl ether $CH_3.CH(NH.CO_2C_3H_7)_2$. [116°]. From propyl carbamate, aldehyde, and a little HCl (Bischoff, *B.* 7, 1082).

ETHYLIDENE CHLORHYDRIN *v.* ω-Chloro-ethyl alcohol.

ETHYLIDENE CHLORIDE $C_2H_4Cl_2$ *i.e.* $CH_3.CHCl_2$. Mol. w. 99. (60·1°) (Thorpe, *C. J.* 37, 183); (56·8°) at 749 mm. (Schiff); (57·3°) (Perkin, *C. J.* 45, 529); (57·5°) (Brühl). V.D. 3·42 (for 3·42) (S.). S.G. $\frac{0}{4}$ 1·2039 (T.); $\frac{9\cdot8}{4}$ 1·1895 (Schiff, *A.* 220, 96); $\frac{15}{15}$ 1·1845; $\frac{25}{25}$ 1·1712 (P.); $\frac{20}{4}$ 1·1743 (Brühl, *A.* 203, 11); 1·1750 (Weegmann, *Z. P. C.* 2, 218). C.E. (0°–10°) ·001304; (0°–50°) ·0013982 (Thorpe); (9·8 to 56·7) ·001438 (Schiff). S.V. 88·96 (Thorpe); 88·56 (Schiff); 89·5 (Ramsay). M.M. 5·335 at 14·4°. μ_D 1·4168 (W.). $\mu_\beta = 1\cdot4223$. R_∞ = 34·10 (B.). H.F.p. 34,230 (*Th.*). H.F.v. 33,070 (*Th.*). *Critical temperature* 255° (Paulewsky, *B.* 16, 2633). By-product in manufacture of chloral (Krämer, *B.* 3, 257).

Formation.—1. By chlorinating ethyl chloride in daylight (Regnault, *A. Ch.* [2] 71, 355), or in presence of heated animal charcoal (Damoiseau, *Bl.* [2] 27, 113).—2. By heating aldehyde with PCl_5 (Wurtz a. Frapolli, *C. R.* 47, 418; *A.* 108, 223; Beilstein, *A.* 113, 110; Geuther, *A.* 105, 321). The PCl_5 is at first kept cool, and the aldehyde added slowly.

Properties.—Colourless oil, resembling chloroform in taste and odour.

Reactions.—1. *Alcoholic potash* has no action in the cold, though vinyl chloride is formed on heating.—2. Aqueous Na_2SO_3 at 140° gives $CH_3.CHCl.SO_3Na$ (Kind, *Z.* [2] 5, 165). Boiling aqueous K_2SO_3 gives $CH_3.CH(SO_3K)_2$ and $CH_3.CH(OH)SO_3K$ (Staedel, *Z.* [2] 4, 272).—3. *Sodium* at 190° gives hydrogen, acetylene, ethylene, ethane, and vinyl chloride (Tollens, *A.* 137, 311).—4. *Chlorine* gives $CH_2Cl.CHCl_2$ and $CH_3.CCl_3$ (Staedel, *B.* 6, 1403).—5. *Bromine* in sunlight forms $CH_3.CBrCl_2$ (99°), $CH_2Br.CBrCl_2$ (177°), and $CHBr_2.CBrCl_2$ (217°) (Staedel, *B.* 11, 1739).—6. *Toluene* and Al_2Cl_6 give *p*-ethyl-toluene, *u*-*p*-di-tolyl-ethane, and *s*-tetra-methyl-anthracene dihydride (Anschütz, *A.* 235, 314). *m*-Xylene, and Al_2Cl_6 give (1,3,4)-ethyl-*m*-xylene and *u*-di-xylyl-ethane.

ETHYLIDENE CHLORO-BROMIDE *v.* Chloro-bromo-ethane.

ETHYLIDENE CHLORO-IODIDE *v.* Chloro-iodo-ethane.

ETHYLIDENE CYANURAMIDE is described under *Cyanuramide v.* Cyanic acid.

ETHYLIDENE-ETHENYL CARBOXYLIC ACID *v.* Butylene carboxylic acid.

ETHYLIDENE DI-ETHYL DIOXIDE is Acetal (*q. v.*).

ETHYLIDENE-DI-ETHYL-DI-SULPHONE $CH_3CH(SO_2Et)_2$. [75°–78°]. Prepared by treating $CH_3.C(SEt)_2.CO_2H$ (obtained from pyruvic acid and mercaptan) with $KMnO_4$ (Escales a. Baumann, *B.* 19, 2814). Plates; sl. sol. water, m. sol. alcohol and ether. Evolves hydrogen when sodium is added to its solution in dry ether or benzene, the resulting salt is too unstable to purify (E. Fromm, *B.* 21, 187). Its bromo- derivative $CH_3.CBr(SO_2Et)_2$ [115°] crystallises in small sparingly soluble prisms which are reconverted by boiling KOHAq into the original $CH_3.CH(SO_2Et)_2$.

ETHYLIDENE IODIDE $CH_3.CHI_2$. (c. 178°). S.G. ^{0} 2·84.

Formation.—1. From ethylidene chloride and Al_2I_6 in CS_2 (Gustavson, *B.* 7, 731).—2. From CH_3CHCl_2 and CaI_2 3½aq at 100° (Spindler, *A.* 231, 267).—3. From acetylene and HI (Berthelot, *A.* 132, 122).

Properties.—Liquid. Converted by alcoholic KOH into vinyl iodide.

ETHYLIDENE-LACTAMIC ACID *v.* α-Imido-di-propionic acid.

ETHYLIDENE-LACTIC ACID *v.* Lactic acid.

ETHYLIDENE-MALONIC ACID $CH_3.CH{:}C(CO_2H)_2$. *Ethyl ether* Et_2A''. (115°–118°) at 17 mm. S.G. ^{15} 1·0435. From malonic ether (1 mol.), aldehyde (2 mols.), and Ac_2O (1½ mols.) at 100° (Komnenos, *A.* 218, 157). (The yield is 54 p.c. of the malonic ether.) Liquid, smelling something like camphor. Aqueous baryta forms various salts, including an easily soluble one, which is possibly a salt of oxethyl-malonic acid, $CH_3.CH(OH).CH(CO_2H)_2$. KOH and dilute alcohol gives β-methyl-glutaric acid.

Ethylidene-di-malonic ether $CH_3.CH(CH(CO_2Et)_2)_2$. (209°–212°) at 20 mm. A by-product in the preparation of ethylidene-malonic ether. (The yield is 8 p.c. of the malonic ether; Komnenos, *A.* 218, 158.) It is formed by the action of ethylidene-malonic ether upon malonic ether: $CH_3.CH{:}C(CO_2Et)_2 + CH_2(CO_2Et)_2 = CH_3.CH(CH(CO_2Et)_2)_2$. Dilute alcoholic KOH converts it into β-methyl-glutaric acid.

ETHYLIDENE-MELAMINE described under *Ethylidene-cyanuramide v.* Cyanic acids.

ETHYLIDENE-METHYL-KETOLE *v.* Di-methyl-ethylidene-di-indole.

ETHYLIDENE-DI-(β)-NAPHTHYL-OXIDE $CH_3.CH\langle{}^{C_{10}H_6}_{C_{10}H_6}\rangle O$. *Anhydride of di-oxy-di-naphthyl-ethane.* [173°]. Crystalline solid. Insol. alkalis. Formed by heating a solution of (β)-naphthol and aldehyde in acetic acid with HCl or H_2SO_4, or by the same treatment of the previously formed di-(β)-naphthyl orthaldehyde $CH_3.CH(O.C_{10}H_7)_2$ (Claisen, *B.* 19, 3318; *A.* 237, 270; *cf.* vol. i. p. 105).

ETHYLIDENE-DIOXAMIDE $C_6H_{10}N_4O_4$ *i.e.* $(NH_2.CO.CO.NH)_2CH.CH_3$. A pulverulent pp. formed when cyanogen is passed into crude aldehyde (Berthelot a. Péan de St. Gilles, *A.* 128, 338; *cf.* Schiff, *A.* 151, 211).

ETHYLIDENE OXY-CHLORIDE *v.* Di-chloro-di-ethyl oxide.

ETHYLIDENE-DI-PHENOL *v.* Di-oxy-di-phenyl-ethane.

ETHYLIDENE-METAPYRAZOLONE *v.* Di-oxy-ethylidene-pyrazole.

ETHYLIDENE SULPHIDE *v.* Thio-acetic aldehyde.

Di-ethylidene-tetra-sulphide $CH_3.CH\langle{}^{S.S}_{S.S}\rangle CH.CH_3$. Formed by oxidation of thialdine by adding to the solution strongly acidified with HCl a weak solution of iodine in KI. Amorphous pp. (Fasbender, *B.* 20, 463).

ETHYLIDENE-THIO-UREA $C_3H_6N_2S$ *i.e.* $CS\langle{}^{NH}_{NH}\rangle CHMe$. From aldehyde and thio-urea at 100° (Emerson Reynolds, *C. N.* 24, 87). Granules, insol. cold water, m. sol. hot alcohol, sl. sol. ether. Boiling water splits it up into aldehyde and thio-urea.

Di-ethylidene-thio-urea. Ammonia compound $(CH_3.CH)_2N_2CSNH_3$. [180°]. Formed by heating a moderately concentrated solution of thio-urea with aldehyde-ammonia (Nencki, *B.* 7, 158). Needles; sl. sol. boiling water, insol. cold alcohol and ether. Its aqueous solution, which is intensely bitter, is resolved by prolonged boiling, or more quickly in presence of acids, into aldehyde, thio-urea, and NH_3.

ETHYLIDENE-TOLUIDINE $CH_3.CH:N.C_6H_4Me$? *Aldehyde-toluide.* Yellow nodules, formed by treating toluidine with aldehyde. Its salts are resinous (Schiff, *Z.* 1865, 400).

ETHYLIDENE-UREA $C_3H_6N_2O$ *i.e.* $CO\langle{}^{NH}_{NH}\rangle CH.CH_3$. [154°]. Formed by the action of an alcoholic solution of aldehyde on urea in the cold (Schiff, *A.* 151, 204). Small needles; v. sl. sol. water and ether, sl. sol. alcohol. Decomposed by heat into NH_3, melanurenic acid, and oxy-trialdine $C_6H_{11}NO$. Rapidly decomposed by pure HNO_3 with evolution of CO_2 and N_2O in equal volumes, together with a little nitrogen (Franchimont, *R. T. C.* 6, 221).

ETHYLIDENE URETHANE *v.* Ethylidene-di-carbamic acid.

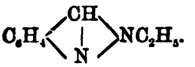
ETHYL-IMIDO-DI-ACETIC ACID $C_6H_{11}NO_4$ *i.e.* $NEt(CH_2.CO_2H)_2$. *Ethyl-di-glycollamic acid.* From ethylamine and chloro-acetic acid (Heintz, *A.* 132, 1; 145, 229). Short trimetric prisms, v. sol. water, sl. sol. alcohol.—CuA″: minute blue dimetric tables, sl. sol. water.

Ethyl ether Et_2A''. (c. 210°). Oil.

ETHYLIMIDO-DI-PHENYLENE SULPHIDE $S(C_6H_4)_2NEt$. *Ethyl-thio-diphenylamine.* [102°]. From imido-diphenylene sulphide and EtBr (Bernthsen, *A.* 230, 93). Prisms. $FeCl_3$ colours its alcoholic solution pale brown.

TRI-ETHYLIN *v.* *Tri-ethyl derivative* of Glycerin.

ETHYL-INDAZINE $C_9H_{10}N$ *i.e.*



$C_6H_4\langle{}^{CH}_{N}\rangle NC_2H_5$. Formed by heating indazine with EtI for four hours at 100°, saturating with NaOH, and extracting with ether (Fischer a. Tafel, *A.* 227, 303). Brown liquid, smelling like indazine; more sol. water than indazine. Is a tertiary base.—$B'H_2SO_4$.

Bromo-ethyl-ψ-indazine $C_9H_{11}N_2Br$. [48°]. Obtained as a sublimate by heating bromo-ethyl-ψ-indazine carboxylic acid, CO_2 being evolved (F. a. T.). V. sl. sol. water, v. sol. alcohol, ether, and chloroform. It shows no basic properties.

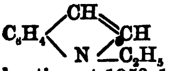
ETHYL-ψ-INDAZYL-ACETIC ACID $C_{11}H_{12}N_2O_2$ *i.e.* $C_6H_4\langle{}^{C(CH_2.CO_2H)}_{NEt\text{———}}\rangle N$. [131°]. Formed by atmospheric oxidation of ethyl-hydrazido-cinnamic acid which is obtained from the nitrosamine of ethyl-*o*-amido-cinnamic acid $NO.NEt.C_6H_4.CH:CH.CO_2H$ by reduction with zinc-dust and acetic acid (Fischer a. Kuzel, *B.* 16, 654; Fischer a. Tafel, *A.* 227, 303). Colourless plates, sol. alcohol, ether, and aqueous alkalis, sl. sol. water. At 100° it splits off CO_2, forming methyl-ethyl-ψ-indazine. It forms salts both with acids and with bases. It does not reduce Fehling's solution or HgO.

Bromo-ethyl-ψ-indazyl-acetic acid $C_{11}H_{11}N_2O_2Br$. [173°]. Formed from the preceding by treatment with Br (65 pts.) in HOAc (Fischer a. Kuzel, *A.* 221, 288). Needles, grouped in fans, v. sol. alcohol and ether, almost insol. water. Oxidation with $K_2Cr_2O_7$ and H_2SO_4 forms bromo-ethyl-ψ-indazine carboxylic aldehyde $C_{10}H_9N_2OBr$ [88°] and, by further oxidation, bromo-ethyl-ψ-indazine carboxylic acid $C_{10}H_9N_2O_2Br$ [210°], which crystallises in needles (from MeOH).

Di-bromo-ethyl-ψ-indazyl-acetic acid $C_{11}H_{10}Br_2N_2O_2$. [196°]. From the acid (1 pt.) and Br (1·7 pts.) in HOAc (5 pts.) in the cold. Stellate groups of needles; almost insol. water, sl. sol. alcohol, ether, and chloroform. Re-converted into the parent acid by sodium amalgam.

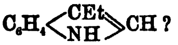
DI-ETHYL-INDIGO $C_{20}H_{18}O_2N_2$ *i.e.* $C_6H_4:C_2O_2N_2Et_2:C_6H_4$. Prepared by reducing the di-ethyl-derivative of pseudo-isatin-ω-oxim $C_6H_4\langle{}^{CO}_{NEt}\rangle C(NOEt)$ with alcoholic ammonium sulphide, and then passing a stream of CO_2 through the solution (Baeyer, *B.* 16, 2201). Blue felted needles. V. sol. alcohol, forming a deep-blue solution, the spectrum of which closely resembles that of indigo. In ether, acetone, chloroform, CS_2, and aniline it is less soluble. It sublimes as a purple vapour, condensing to blue prisms. It dissolves in strong H_2SO_4 with a greenish-blue colour, and on heating is sulphonated. With zinc-dust and alkalis it is reduced, and the solution then dyes like indigo. On oxidation it gives ethyl-pseudo-isatin. By weak reduction the di-ethyl-derivative of pseudo-isatin-*ω*-oxim is formed.

ETHYL-INDOLE $C_{10}H_{11}N$ *i.e.*



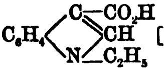
(about 247°). Obtained by heating at 185°–190° the carboxylic acid [183°] which is formed by the action of HCl on phenyl-ethyl-hydrazine-pyruvic acid (Fischer a. Hess, *B.* 17, 566). Liquid. The HCl solution gives a violet colour to a pine-wood shaving. By a cold alkaline solution of chlorine, followed by hot alcoholic NaOH, it is converted into ethyl-pseudo-isatin. The picrate forms red needles.

Ethyl-indole?



$C_6H_4{<}{\begin{smallmatrix}CEt\\NH\end{smallmatrix}}{>}CH$? (283° cor.). Formed by heating aniline (30 g.) with $ZnCl_2$ (50 g.), lactic acid (35 g.), and sand to prevent frothing (Pictet a. Duparc, *B.* 20, 3415). Yellow oil without basic character, v. sl. sol. water, v. sol. alcohol, ether, benzene, and $CHCl_3$. May be distilled with steam. Colours pinewood moistened with HCl red. Bromine added to its solution in chloroform gives an intense violet colour. The picrate melts at [143°].

ETHYL-INDOLE-CARBOXYLIC ACID $C_{11}H_{11}NO_2$ *i.e.*



[183°]. Formed by the action of hot aqueous HCl on phenyl-ethyl-hydrazine-pyruvic acid (for theory of reaction *v.* under INDOLE derivatives) (Fischer a. Hess, *B.* 17, 565). Colourless needles. V. sol. alcohol, ether, benzene, and chloroform, less sol. water. Heated to its melting-point for some time it loses CO_2, giving ethyl-indole. A cold alkaline solution of chlorine, followed by alcoholic NaOH, converts it into ethyl-pseudo-isatin.

ETHYL-INDOXYL *v.* INDOXYL.

ETHYL-INDOXYLIC ACID *v.* INDOXYLIC ACID.

ETHYL-DI-IODAMINE *v.* ETHYLAMINE.

ETHYL IODIDE C_2H_5I. Mol. w. 156. (72°) (Schiff); (72·4°) (Perkin, *C. J.* 45, 460). S.G. $\frac{15}{15}$ 1·9433; $\frac{25}{25}$ 1·9243 (P.); $\frac{0}{0}$ 1·9795 (Dobriner, *A.* 243, 24). C.E. (0°–10°) ·00116 (D.). S.V. 86·12 (S.); 85·6 (D.). V.D. 5·48 (calc. 5·41). M.M. 10·075 at 18·1° (P.). H.F.p. 5,660 (Iodine solid); 11,090 (I gaseous) (*Th.*); 7,000 (I gaseous, EtI gaseous) (Berthelot); 12,700 (I solid, EtI liquid) (B.). H.F.v. 4,790 (I solid); 9,930 (I gaseous) (*Th.*). Formed by distilling alcohol with HI containing free I, or by the action of P and I on alcohol (Gay-Lussac, *A. Ch.* 91, 89; Serullas, *A. Ch.* [2] 25, 323; 42, 119; Marchand, *J. pr.* 33, 186; Frankland, *C. J.* 2, 263; 3, 322; Lautemann, *A.* 113, 241; Hofmann, *C. J.* 13, 69; De Vrij, *J. Ph.* [3] 31, 169; Paterno, *G.* 4, 149; H. Schiff, *B.* 7, 592; Personne, *C. R.* 52, 468). The rate at which HI etherifies alcohol has been studied by Villiers (*C. R.* 90, 1563; 91, 62).

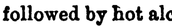
Preparation.—1. Amorphous phosphorus (10 pts.), alcohol (50 pts. of 90 p.c.), and iodine (100 pts.), are mixed and left to themselves for 24 hours; the mixture is then distilled (Rieth a. Beilstein, *A.* 126, 250).—2. An alcoholic solution of iodine is slowly run into a retort containing alcohol and clear phosphorus (Hofmann).

Properties.—Colourless liquid. Not very inflammable. When not quite pure it turns brown in light. Conc. HNO_3 liberates iodine. Aqueous KOH has little action. When a soluble salt of silver is added to an alcoholic solution of EtI silver iodide is ppd.

Reactions.—1. Passage through a *red-hot tube* gives hydrogen, ethylene, and ethylene iodide (E. Kopp, *J. Pharm.* [3] 6, 109).—2. *Mercury* forms EtHgI.—3. Heating with $ZnEt_2$ in ethereal solution at 170° gives butane, together with a little ethylene and ethane (Brodie, *C. J.* 3, 405).—4. *Sodium ethide* gives ethylene and ethane in the cold.—5. *Tin* at 180° gives $SnEt_2I_2$ (Frankland, *C. J.* 6, 57).—6. *Silver powder* at 120° gives butane (Wislicenus, *Z.* [2] 4, 681).—7. By heating in sealed tubes with excess of *zinc* there is formed zinc ethide; when excess of EtI is used the product is butane.—8. The *copper zinc couple* at 100° forms IZnEt. In presence of water or alcohol ethane is evolved (Gladstone a. Tribe, *C. J.* 26, 445).—9. Alcoholic *ammonia* forms iodides of ammonium and of mono-, di-, tri-, and tetra- ethyl-ammonium.—10. When saturated with PH_3 and heated, either alone or with ZnO, there is formed tri- and tetra- ethyl-phosphonium iodide (Hofmann, *B.* 4, 372).—11. *Chromic acid mixture* gives iodine and acetic acid.—12. *Chlorine* gives EtCl and I (Dumas a. Stas, *A.* 35, 162).—13. *Bromine* gives EtBr and I (Friedel, *C. R.* 60, 346).—14. ICl gives EtCl and I (Geuther, *A.* 123, 123).—15. HI at 150° forms some ethane (Butlerow, *A.* 144, 36).—16. Heating with $HgCl_2$ gives EtCl (Oppenheim, *C. R.* 62, 1085).—17. Heating with K_2SO_3 gives potassium ethane sulphonate $EtSO_3K$ (Strecker, *Z.* [2] 4, 213).—18. *Sodium amalgam* acting on a moist mixture of EtI with CS_2 forms Et_2CS_3 (Nasini a. Scala, *G.* 17, 236; *cf.* Löwig a. Scholz, *J. pr.* 79, 441).—19. *Water* at 150° gives ether (Reynoso, *A. Ch.* [3] 48, 385).

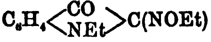
ETHYL-ISATIN $C_{10}H_9NO_2$. [137°]. Long red needles (Paucksch, *B.* 17, 2805). Formed by heating with HClAq the product of the action of di-chloro-acetic acid on *p*-amido-phenyl-ethane $C_6H_4Et(NH_2)[1:4]$.

Ethyl-pseudo-isatin



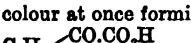
$C_6H_4{<}{\begin{smallmatrix}CO\\NEt\end{smallmatrix}}{>}CO$. *Lactam of ethyl isatic acid.* [95°].

Formation.—1. By the action of a cold alkaline solution of chlorine followed by hot alcoholic NaOH on ethyl-indole-carboxylic acid [183°], which is obtained by the action of HCl on phenyl-ethyl-hydrazine-pyruvic acid (Fischer a. Hess, *B.* 17, 566).—2. By reduction of the di-ethyl-derivative of pseudo-isatin-*ω*-oxim



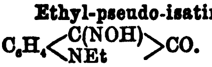
$C_6H_4{<}{\begin{smallmatrix}CO\\NEt\end{smallmatrix}}{>}C(NOEt)$ with zinc-dust and oxidation of the product with Fe_2Cl_6 (Baeyer, *B.* 16, 2193).

Properties.—Large red plates. Soluble in hot water, alcohol and ether. With thiophene and H_2SO_4 it gives a blue colouring-matter soluble in ether. It dissolves in alkalis with a yellow colour at once forming a salt of ethyl-isatic acid



$C_6H_4{<}{\begin{smallmatrix}CO.CO_2H\\NHEt\end{smallmatrix}}$.

Ethyl-pseudo-isatin-*α*-oxim



$C_6H_4{<}{\begin{smallmatrix}C(NOH)\\NEt\end{smallmatrix}}{>}CO$. [162°]. Yellow four-sided prisms. Formed by the action of hydroxylamine on ethyl-pseudo-isatin. On reduction with zinc-dust followed by oxidation with Fe_2Cl_6 it yields ethyl-pseudo-isatin. It does not yield indigo on treatment with ammonium sulphide (Baeyer, *B.* 16, 2196).

Ethyl-pseudo-isatin-α-ethyloxim *v.* *Di-ethyl-derivative* of *pseudo*-Isatin-ω-oxim.

ETHYL-KAIRINE *v.* *Ethyl ether* of (*B.* 4)-Oxy-(*Py.* 4)-ethyl-quinoline tetrahydride.

DI-ETHYL-KETINE *v.* Di-methyl-di-ethyl pyrazine.

DI-ETHYL-KETONE $C_5H_{10}O$ *i.e.* Et.CO.Et. *Propione. Metacetone.* Mol. w. 86. (101°). S.G. ^{0} ·829; $\frac{17·5}{}$·815. S. 4·2. H.C. 735,971 (Louguinine, *Bl.* [2] 41, 389). A product of the distillation of sugar, starch, or mannite with lime (Fremy).

Formation.—1. By the dry distillation of barium propionate (R. Morley, *A.* 78, 187).—2. By the action of $ZnEt_2$ on propionyl chloride (Freund a. Pebal, *A.* 118, 9).—3. From sodium ethide and CO (Wanklyn, *A.* 140, 211).—4. By oxidising oxy-hexoic acid (di-eth-oxalic acid) with $K_2Cr_2O_7$ and H_2SO_4 (Chapman a. Smith, *C. J.* 20, 173); or by heating the ether of the same acid for several hours with fuming HCl at 150° (Geuther, *Z.* 1867, 709).—5. By oxidation of di-ethyl-carbinol $Et_2CH(OH)$ (Wagner a. Saytzeff, *A.* 179, 322).—6. By the action of dry $FeCl_3$ on propionyl chloride (Hamonet, *Bl.* [2] 50, 547).

Properties.—Mobile oil, lighter than water, v. sol. alcohol and ether. Smells like acetone. Slowly combines with $KHSO_3$ on long agitation (Schramm, *B.* 16, 1583). Chromic acid mixture oxidises it to propionic, acetic, and carbonic acids. Reduced by sodium in presence of water to di-ethyl-carbinol and the pinacone $C_{10}H_{20}(OH)_2$. Treated with di-methyl-aniline and $ZnCl_2$ there is formed tetra-methyl-di-amido-di-phenyl-methane (Dobner a. Petschoff, *A.* 242, 333). Treatment with Zn, EtI, and then with water gives tri ethyl-carbinol (A. Saytzeff, *J. pr.* [2] 31, 320).

Cyanhydrin $Et_2C(OH).CN$. *α-Oxy-hexo-nitrile.* From the ketone and dilute HCN (Tiemann a. Kohler, *B.* 14, 1978). Liquid, lighter than water.

Oxim $Et_2C{:}NOH$. (163°) at 726 mm. From di-ethyl-ketone and an alcoholic solution of hydroxylamine (Scholl, *B.* 21, 509). Oil, insol. water, sol. alcohol and ether. When dissolved in ether and treated with N_2O_4 it gives amyl-pseudo-nitrole $Et_2C(NO).NO_2$ in the form of large tables [63°], which forms blue solutions in ether and chloroform.

DI-ETHYL-KETONE DI-CARBOXYLIC ACID $C_7H_{10}O_5$ *i.e.* $CO(CH_2.CH_2.CO_2H)_2$. [138°] and [c. 110°]. Formed by saponifying its ether. Thin plates, decomposed on distillation. Not reduced by sodium-amalgam. Does not combine with Br. HNO_3 oxidises it to succinic acid.—Ag_2A'': minute needles.

Mono-ethyl ether EtHA''. [68°]. From Et_2A'' (1 mol.) and alcoholic KOH (1 mol.). Needles, insol. ligroin, sol. water, alcohol, ether, and chloroform.—AgEtA''.

Di-ethyl ether Et_2A''. (286°). Formed by heating furfuryl-acrylic acid with alcohol saturated with HCl (Marckwald, *B.* 20, 2811; 21, 1398). Heavy oil. Alcoholic NH_3 forms $C_7H_{10}O_2N_2$ [292°].

Oxim of the di-ethyl ether $HO.N{:}C(CH_2.CH_2.CO_2Et)_2$. [38°]. Slender needles, sl. sol. water.

Phenyl-hydrazide $N_2HPh.C(C_2H_4.CO_2H)_2$. [114·5°]. Minute pale yellow crystals, insol. water, benzene, and light petroleum, sol. alcohol and ether. Heating at 210° with HIAq (S.G. 1·7) and amorphous phosphorus reduces it to *n*-pimelic acid.

Phenyl-hydrazide of the mono-ethyl ether $N_2HPh.C(C_2H_4.CO_2H)(C_2H_4.CO_2Et)$. [112°]. Minute pale yellow crystals, insol. water and light petroleum, v. sol. hot alcohol and ether.

TETRA-ETHYL LEUCANILINE *v.* Tetra-ethyl-tri-*p*-amido-tri-phenyl-methane.

ETHYL-LEUCAZONE *v.* Azaurolic acid.

DI-ETHYL-MALEIC ACID $C_8H_{12}O_4$ *i.e.* $CO_2H.CEt{:}CEt.CO_2H$. *Xeronic acid.* The anhydride occurs among the products of the distillation of citric acid, being formed by boiling citraconic anhydride for a long time. This anhydride is converted into the Ca salt by digestion with water and $CaCO_3$ (Fittig, *A.* 188, 59). Formed also by treating αα-di-bromo-butyric acid with reduced silver (Otto a. Beckurts, *A.* 239, 277). The free acid, liberated by adding HCl to its salts, changes at once into the anhydride. It does not combine with Br. HI reduces it to di-ethyl-succinic acid. Chromic acid mixture oxidises it to propionic acid (Roser, *B.* 15, 1321).

Salts.—Ag_2A''. — CuA''aq. — CaA''aq. — BaA'' ½aq.

Anhydride $C_8H_{10}O_3$. (242° i.V.). Liquid; volatile with steam. Sl. sol. cold water.

ETHYL-MALONIC ACID $C_5H_8O_4$ *i.e.* $CHEt(CO_2H)_2$. Mol. w. 132. [112°].

Formation.—1. By treating α-bromo-*n*-butyric acid with KCy and boiling the product with potash (Wislicenus, *A.* 149, 220; 165, 93; Tupoleff, *A.* 171, 243; Markownikoff, *A.* 182, 324). 2. By heating malonic ether (16 pts.), and sodium (2 pts.) dissolved in alcohol (25 pts.) with gradual addition of EtI (20 pts.). The resulting ether is saponified by potash, neutralised by HCl, and converted into the Ca salt. The Ca salt is then decomposed by HCl and the acid extracted with ether (Conrad, *A.* 204, 134).

Properties. — Short four-sided prisms or feathery groups. V. sol. water, alcohol, and ether. At 160° it splits up into CO_2 and butyric acid. The same decomposition occurs when its aqueous solution is evaporated at too high a temperature, especially in presence of mineral acids. Fe_2Cl_6 gives no pp. in neutral solutions.

Salts.—K_2A'' *x*aq: small crystals, v. sol. water, insol. alcohol.—Na_2A'' *x*aq: efflorescent granular mass.—BaA'': small needles.—CaA''aq: prisms; sl. sol. hot, v. sol. cold, water.—ZnA'' 2½aq: crystalline powder composed of minute six-sided plates; S. ·22.—ZnA'' 3aq.—CuA'' 3aq: bluish-green tablets.—PbA'': white pp. becoming granular on boiling.—Ag_2A'': sparingly soluble needles.—The aniline salt when treated in benzene with phosphorus pentachloride gives PhN:CH.O.CClEt.CONHPh [104°], (*Py.* 1)-chloro-(*Py.* 3)-oxy-(*Py.* 2)-ethyl-quinoline [248°], and the anilide of di-chloro-butyric acid [200°] (Rugheimer a. Schramm, *B.* 21, 304).—The *o*-toluidine salt gives with PCl_5 (*Py.* 1)-chloro-(*Py.* 3)-oxy-(*Py.* 2)-ethyl-(*B.* 4)-methyl-quinoline (R. a. S.) [225°].

Di-ethyl ether Et_2A''. (200° uncor.); (210° cor.). S.G. $\frac{15}{15}$ 1·0124; $\frac{25}{25}$ 1·0044. M.M. 9·272 at 15·5° (Perkin, *C. J.* 45, 512). From the silver salt and EtI. Prepared also by the action of EtI (1 mol.) on a mixture of malonic ether (1 mol.) and NaOEt (1 mol.) (Conrad, *B.* 12, 751; *A.* 204, 134). Formed also by heating malonic ether with EtI and zinc (Schukoffsky, *J. R.* 1887, 601). Above 250° it is partially decomposed with formation of butyric ether. Iodine appears to convert sodium ethyl-malonic ether into $C_2H_5.CI(CO_2Et)_2$, whence alcoholic KOH forms $Et.C(OEt)(CO_2K)_2$, while baryta-water forms barium ethyl-tartronate (Bischoff a. Hausdörfer, *A.* 239, 120).

Amide $CHEt(CONH_2)_2$. [208°]. From the ether and NH_3 (Freund a. Goldsmith, *B.* 21, 1243).

Amide-anilide $CHEt(CONH_2)(CONHPh)$. [182°]. Formed by heating the amide (1 mol.) with aniline (1 mol.).

Anilide $CHEt(CONHPh)_2$. [215°] (F. a. G.); [223°] (Rügheimer, *B.* 17, 235). Needles (from alcohol). Formed by heating the amide (1 mol.), the acid, or the ether, with aniline (2 mols.).

Mono-anilide $CHEt(CONHPh)(CO_2H)$. [150°]. Formed by boiling the preceding with excess of lime (F. a. G.).

Phenyl-hydrazide $CHEt(CO.NH.NHPh)_2$. [233°]. Obtained by heating the amide with phenyl-hydrazine (F. a. G.). Needles (from HOAc); insol. water, sl. sol. alcohol. $COCl_2$ converts it into $C_{19}H_{16}N_4O_4$ [above 300°].

Di-ethyl-malonic acid $C_7H_{12}O_4$ *i.e.* $CEt_2(CO_2H)_2$. [121°]. S. 65 at 16°. Formed by treating malonic ether with NaOEt (2 mols.) and EtI (2 mols.), and saponifying the product (Conrad, *A.* 204, 138). Prisms; v. sol. alcohol and ether. At 170° it splits up into CO_2 and $CHEt_2.CO_2H$.

Salts.—CaA″: moderately soluble crystalline pp.—Ag_2A'': crystalline pp.

Ethyl ether Et_2A''. (230° cor.). S.G. $\frac{15}{15}$ ·9917; $\frac{25}{25}$ ·9844. M.M. 11·20 at 19° (Perkin, *C. J.* 45, 513). Formed as above. Formed also by treating malonic ether with $ZnEt_2$ (Martinoff a. Schukoffsky, *J. R.* 1887, 297).

References.—Chloro- and Bromo- ethyl-malonic acid and ether.

ETHYL-MALONYL-UREA *v. Ethyl-derivative* of Barbituric acid.

ETHYL-MELAMINE. Described as *Ethyl-cyanuramide v.* Cyanic acid.

ETHYL MERCAPTAN *v.* Mercaptan.

ETHYL-METHYL- *v.* Methyl-ethyl-.

ETHYL-METHYLENE- *v.* Methylene-ethyl-.

ETHYL MUSTARD OIL *v.* Ethyl thio-carbimide.

(α) - ETHYL - NAPHTHALENE $C_{12}H_{12}$ *i.e.* $C_{10}H_7.C_2H_5$. (259° i.V.); (100° at 4 mm.). V.D. 5·35 (obs.). S.G. $\frac{0}{0}$ 1·0204; $\frac{20}{0}$ 1·0123. Prepared by the action of sodium on a mixture of (α)-bromo-naphthalene and ethyl bromide (Fittig a. Remsen, *Z.* [2] 5, 37; *A.* 155, 118). Colourless liquid. Partially decomposed on distillation. Br gives a tri-bromo- derivative [127°].—Picric acid compound: fine yellow needles [98°] (Carnelutti, *B.* 13, 1671; *G.* 10, 388).

(β)-Ethyl-naphthalene $C_{10}H_7Et$. (251°). S.G. $\frac{0}{0}$ 1·0078. Colourless liquid. Solidifies at −19°. Prepared by the action of sodium on a mixture of (β)-bromo-naphthalene and ethyl bromide (Brunel, *B.* 17, 1179). It is also formed (probably together with the (α)-ethyl-naphthalene) by the action of Al_2Cl_6 on a mixture of naphthalene (100 pts.) and ethyl bromide or chloride (50 pts.) (Marchetti, *G.* 11, 265, 439). EtBr gives the best yield (Roux, *A. Ch.* [2] 12, 289).—Picric acid compound: [69°] (B.); [71°] (M.); yellow needles or long plates.

(α) - ETHYL - NAPHTHALENE SULPHONIC ACID $C_{12}H_{11}SO_3H$. Forms an amorphous Ba salt and a crystalline copper salt $CuA'_2 2aq$, m. sol. water.

(β)-Ethyl-naphthalene sulphonic acid $C_{12}H_{11}SO_3H$. From (β)-ethyl-naphthalene and H_2SO_4. Forms a lead salt PbA'_2, crystallising in scales (Marchetti, *G.* 11, 439).

ETHYL-NAPHTHOIC ACID. *Amide* $C_{10}H_6Et.CONH_2$ [1:4]. [166°]. Formed by acting on (α)-ethyl naphthaline with chloro-formic amide in presence of Al_2Cl_6 (Gattermann, *A.* 244, 57). Colourless needles (from alcohol). On hydrolysis (1·4) ethyl-naphthoic acid [132°] is obtained.

(β)-ETHYL-NAPHTHOL $C_{10}H_6Et.OH$. [98°]. Obtained by fusing (β)-ethyl-naphthalene sulphonic acid with potash (Marchetti, *G.* 11, 442). Silvery leaflets, insol. cold water, v. sol. alcohol and ether.

ETHYL-NAPHTHYL-AMINE *v.* Naphthyl-ethyl-amine.

ETHYL - NAPHTHYLENE - DIAMINE *v.* Naphthylene-ethyl-diamine.

ETHYL NITRATE $C_2H_5NO_3$. *Nitric ether.* Mol. w. 91. (86°) at 728 mm. S.G. $\frac{0}{}$ 1·132; $\frac{15·5}{}$ 1·112 (Kopp, *A.* 98, 367). H.F.p. 40,780 (*Th.*); 30700 (Berthelot). H.F.v. 38,750 (*Th.*). S.V. 91·1 (Ramsay). Formed by distilling alcohol with an equal weight of HNO_3 (S.G. 1·4) containing 3 p.c. of urea; the distillation must be stopped when two-thirds of the liquid has distilled over, otherwise an explosive reaction will set in (Millon, *A. Ch.* [3] 8, 239; Carey Lea, *Am. S.* [2] 32, 178). It may also be obtained by dropping absolute alcohol (10 g.) from a very fine pipette into conc. HNO_3 (20 g.) cooled with ice and salt (Persoz, *Rép. Chim. pure*, 5, 30). Alcoholic $AgNO_3$ boiled with EtI or EtBr does not yield ethyl nitrate, but aldehyde and ethyl nitrite. The $EtNO_3$ may be supposed to be reduced by the alcohol at the moment of formation thus: $EtNO_3 + C_2H_5.OH = EtNO_2 + C_2H_4O + H_2O$ (Bertrand, *Bl.* [2] 33, 566).

Preparation.—A mixture of alcohol (300 g.), urea nitrate (100 g.), and HNO_3 (400 g. of S.G. 1·4) is distilled to half its volume, after which a mixture of alcohol (3 pts.) and nitric acid (4 pts.) is run in slowly so as to keep the level of the liquid constant. The nitric acid used must have been previously heated to boiling with 1 p.c. of urea and afterwards cooled (Lossen, *A. Suppl.* 6, 220; Bertoni, *G.* 6, 406).

Properties.—Colourless oil with pleasant odour and sweet taste; miscible with alcohol and ether. It burns with a white flame.

Reactions.—1. Alcoholic NH_3 at 100° gives ethylamine nitrate NEt_3HNO_3 (Juncadella, *C. R.* 48, 342). A mixture of nitric ether (1 vol.), alcohol (1 vol.), and conc. NH_3Aq (1 vol.) at 100° forms mono-, di-, and tri-, ethylamine (Lea).—2. *Ammonium sulphide* in alcoholic solution yields mercaptan (E. Kopp, *J. Ph.* [3] 11, 321).

3. Tin and HCl reduce it to hydroxylamine and di-ethyl-hydroxylamine (Lossen). — 4. When heated with ferrous acetate nitrogen is given off (Lea).

ETHYL NITRITE $C_2H_5NO_2$ *i.e.* Et.O.NO. *Nitrous ether.* Mol. w. 75. (18°). S. 2. S.G. $\frac{0}{0}$ ·919; $\frac{15\cdot5}{}$ ·900 (Brown, *Ph.* 15, 400). H.F.p. 30,610. H.F.v. 28,870. Produced by the action of nitric acid upon alcohol. The reaction is very violent, the alcohol being oxidised to aldehyde, &c., while the nitric acid is reduced to nitrous acid which etherifies the remaining alcohol (Kunkel, A.D. 1681; Dumas a. Boullay, *A. Ch.* [2] 37, 15). 'Sweet spirit of nitre' is obtained by distilling an excess of alcohol with HNO_3. Alcohol may be saved by adding copper, starch, or sugar to the mixture; or the ether may be obtained by passing nitrous fumes into alcohol (Liebig, *A.* 30, 142; E. Kopp, *J. Ph.* [3] 9, 320; Grant, *Ph.* 10, 244; Feldhaus, *A.* 126, 71).

Preparation.—34·5 g. $NaNO_2$ dissolved in 120 c.c. of water are cooled below 0°; 13·5 c.c. H_2SO_4 are added to 32 c.c. rectified spirit mixed with an equal volume of water, and the mixture diluted to 120 c.c. and cooled. The acid mixture is added gradually to the nitrite solution and the ether separated by a tap funnel, washed with water, and dried over ignited K_2CO_3. Glycerin (5 p.c.) added to the 2 p.c. alcoholic solution prevents its decomposition (Dunstan a. Dymond, *Ph.* 18, 861).

Properties.—Liquid, with characteristic odour; miscible with alcohol, sl. sol. water. Decomposes when kept in a wet state, giving off NO. Saponified by solid KOH giving KNO_2 and alcohol (Liebig a. Strecker, *A.* 77, 331). Reduced by H_2S or ammonium sulphide to alcohol and NH_3. Diazotises aromatic amido- compounds.

ETHYL-NITRO- *v.* NITRO-ETHYL-.

ETHYL-NITROLIC ACID $C_2H_4N_2O_3$ *i.e.* $CH_3.C(NO_2):NOH$ or $CH_3.CH(NO_2).NO$. [82°].

Formation.—1. By the action of potassium nitrite and H_2SO_4 on an alkaline solution of nitro-ethane (V. Meyer, *B.* 6, 1494; 7, 425; *A.* 180, 170).—2. From di-bromo-nitro-ethane and hydroxylamine in the cold.

Preparation.—From nitro-ethane (6 c.c.), ice, potash (15 c.c., containing 6·7 g. KOH), and $NaNO_2$ (15 c.c. containing 8 g.). Dilute H_2SO_4 is added, and the product extracted by ether (v. Meyer a. E. J. Constam, *A.* 214, 329).

Properties.—Light-yellow transparent trimetric prisms resembling KNO_3. Tastes sweet, and has an acid reaction. V. e. sol. warm, sl. sol. cold, water. Dissolves in aqueous alkalis and in baryta, giving a deep red solution. An ethereal solution is not coloured by dry NH_3 until water is added. Lead acetate gives a brilliant orange pp., $AgNO_3$ gives an egg-yellow pp.

Reactions.—1. When *heated* to 82° it melts, and is completely decomposed, thus:

$$2CH_3.C(NO_2):NOH = 2CH_3.CO_2H + N_2 + NO_2.$$

The same decomposition occurs slowly in the cold, and quickly on boiling with an alkali.—2. *Sodium amalgam* reduces it to acetic acid, nitrous acid, and NH_3. Tin and HCl act in the same way. In the case of sodium amalgam, ethyl-azaurolic acid is an intermediate product.—3. Conc. *sulphuric acid* splits it up into acetic acid and N_2O.

Isomeride of ethyl-nitrolic acid $C_2H_4N_2O_3$. [75°]. Formed by the action of sodium amalgam upon nitro-ethane (Kissel, *Bl.* [2] 40, 72; *J. R.* 15, 91). Prisms or needles (from chloroform). Acid in reaction, and forms salts with alkalis, but their solutions are not red.

ETHYL-NITRO-PHENYL- *v.* NITRO-PHENYL-ETHYL-.

DI-ETHYL-NITROSAMINE *v.* DI-ETHYL-AMINE.

DI-ETHYL-ISO-NITROSO-AMYL-AMINE $NEt_2(C_5H_9NOH)$. [72°]. Large flat crystals obtained by acting on Guthrie's amylene nitrite with diethylamine (Wallach, *A.* 241, 304).

ETHYL *n*-OCTYL OXIDE $Et.O.C_8H_{17}$. (189·2°). S.G. $\frac{0}{0}$ ·8008. S.V. 244·9. C.E. (0°–10°) ·00101 (Dobriner, *A.* 243, 6). (183°). S.G. $\frac{17}{}$ ·805 (Möslinger, *A.* 185, 57).

ETHYL-OXALIC ACID *v.* OXALIC ACID.

Di-ethyl-oxalic acid *v.* OXY-HEXOIC ACID.

ETHYL-OXALYL-ANTHRANILIC ACID *v.* CARBOXY-PHENYL-OXAMIC ACID.

ETHYL-OXAMIC ACID $C_4H_7NO_3$ *i.e.* $NHEt.CO.CO_2H$. [120°]. Formed by heating the acid oxalate of ethylamine (Wurtz, *A. Ch.* [3] 30, 443). Its ether is obtained by treating oxalic ether with ethylamine, and may be saponified by boiling water or by milk of lime (Wallach a. West, *B.* 8, 760; *A.* 184, 58; *cf.* Heintz, *A.* 127, 43). Six-sided tables, v. sol. water, alcohol, and ether. May be extracted from its aqueous solution by ether. Sublimes in woolly needles. Cold conc. KOHAq decomposes it, giving off ethylamine. Boiling NH_3Aq does not act on it.—CaA'_2 2aq: prisms.—CaA'_2 4aq (Duvillier a. Buisine, *A. Ch.* [5] 23, 349). S. 3·17 at 17·5°.—BaA'_2 aq.

Ethyl ether EtA'. *Ethyl-oxamethane.* (245°). Formed as above. Liquid, miscible with water, alcohol, and ether. Saponified by hot water. NH_3 converts it into ethyl-oxamide $NHEt.CO.CO.NH_2$. PCl_5 gives crystalline $CO_2Et.CCl_2.NHEt$ [above 50°], which is slowly decomposed at 100°, giving off EtCl and CO_2.

Di-ethyl-oxamic acid $NEt_2.CO.CO_2H$. [101°]. Prepared by saponification of the ether (Wallach, *B.* 14, 743; *A.* 214, 270). Large monoclinic prisms. V. sol. water and alcohol. Split up by heat into CO_2 and di-ethyl-formamide. PCl_5 forms $NEt_2.CO.COCl$.—CaA'_2 2aq: v. e. sol. water and boiling alcohol.

Ethyl ether EtA'. (252°). Formed by treating oxalic ether with diethylamine (Hofmann, *Pr.* 11, 66; *B.* 3, 779; Heintz, *A.* 127, 52).

Nitrile $NEt_2.CO.CN$. (220°). From unsymmetrical di-ethyl-oxamide, $NEt_2CO.CONH_2$, and P_2O_5 (Wallach, *A.* 214, 264). Liquid. Sl. sol. water. Volatile with steam. Lighter than water. Gives with PCl_5 a little chloro-oxal-ethyline.

ETHYL-OXAMIDE $C_4H_8N_2O_2$ *i.e.* $NH_2.CO.CO.NHEt$. [203°]. From ethyloxamic ether and NH_3, or from oxamic ether and ethylamine (Wallach, *A.* 184, 65). Flexible needles; may be sublimed. V. sol. hot water.

***u*-Di-ethyl-oxamide** $CONH_2.CONEt_2$. [127°]. (267° cor.). From diethyl-oxamic ether and cold aqueous NH_3 (Wallach, *A.* 214, 260). Long prisms; sublimes at 100°. Sol. hot water and alcohol. Converted by PCl_5 into chloro-oxal-ethyline $C_6H_9ClN_2$. (Yield, bad.)

s-**Di-ethyl-oxamide** CO(NHEt).CO.NHEt. [175°] (Wallach, *A.* 214, 268); [179°] (Schiff, *B.* 17, 1034). S.G. $\frac{4}{4}$ 1·169 (Schröder, *B.* 12, 1611). From oxalic ether and aqueous ethylamine (Wurtz, *A. Ch.* [3] 30, 490). Needles. More soluble in water and alcohol than oxamide. May be sublimed in crystals. Potash converts it into ethylamine and oxalic acid.

Triethyl-oxamide $NHEt.CO.CO.NEt_2$. (258°). Obtained from strong aqueous ethylamine solution and diethyl-oxamic ether $NEt_2.CO.COOEt$. Liquid; miscible with water; decomposed by PCl_5 (Wallach, *A.* 214, 267).

ETHYL-OXANTHRANOL *v.* OXANTHRANOL.

DI-ETHYL-OXETHYL-AMINE *v.* OXY-TRI-ETHYL-AMINE.

DI-ETHYL OXIDE *v.* ETHER.

Ethyl peroxide $(C_2H_5)_4O_3$ (?) Obtained by passing a slow current of dry ozonised oxygen over dry ether (Berthelot, *C. R.* 92, 895; *A. Ch.* [5] 27, 229). Syrupy liquid; does not solidify at −40°. Explodes when distilled. Decomposed by water into alcohol and H_2O_2.

ETHYL-OXINDOLE *v.* OXINDOLE.

ETHYL-OXY- *v. Ethyl derivatives* of OXY-.

DI-ETHYL-OXYALLYL-AMINE $NEt_2.C_3H_4OH$. (c. 160°). The most volatile of the bases obtained by the action of epichlorhydrin on di-ethyl-amine (Reboul, *C. R.* 97, 1488, 1556). Thick liquid with powerful odour resembling that of diethylamine. V. sol. water. HCl followed by $PtCl_4$ gives $\{NEt_2C_3H_5Cl(OH)\}_2H_2PtCl_6$ crystallising in garnet-red prisms; the corresponding base $NEt_2.C_3H_5Cl(OH)$ is the first product of the action of NEt_2H on epichlorhydrin.

ETHYL-OXY-PROPYL-AMINE $(C_3H_6.OH)(C_2H_5)NH$. (c. 160°). Formed by heating ethyl-allyl-amine with H_2SO_4 and pouring the product into water.—$B'_2H_2Cl_2PtCl_4$ 2aq: v. sol. water (Liebermann, *B.* 16, 531).

Oxy-propyl-di-ethyl-amine C_7H_7ON *i.e.* $CH_2(OH).CH_2.CH_2.N(C_2H_5)_2$. *Trimethylene-di-ethylalkine.* (190°). S.G. $\frac{4}{4}$ = ·9199. Colourless liquid. Miscible with water. Formed by heating trimethylene-chlorhydrin with di-ethyl-amine. The platino-chloride forms very soluble orange-red prisms; the aurochloride forms thick plates; the picrate long soluble needles (Berend, *B.* 17, 512).

Di-ethyl-oxypropyl-amine $C_7H_{17}NO$. (159°). *Di-ethyl-propyl-alkine.* Prepared by the action of diethylamine on propylene-chlorhydrin. $(B'HCl)_2PtCl_4$. V. sol. water (Ladenburg, *B.* 14, 2407).

Di-ethyl-di-oxypropyl-amine $C_7H_{17}NO_2$ *i.e.* $NEt_2.CH_2.CH(OH).CH_2OH$. *Di-ethyl-propyl-glycolline.* (234°). Colourless oil. Soluble in water, alcohol, and ether. Formed by heating di-ethyl-amine with glycerine-chlorhydrin.—$B_2H_2Cl_2PtCl_4$: reddish-yellow tables (Roth, *B.* 15, 1151).

Benzoyl derivative $NEt_2.CH_2.CH(OH).CH_2(OBz)$. Thick liquid. Its picrate $C_{14}H_{21}NO_3C_6H_2(OH)(NO_2)_3$ crystallises in yellow plates; v. sl. sol. water.

ETHYL-OXYPROPYL-ANILINE $C_6H_5.N(C_2H_5)(C_3H_6.OH)$. *Ethyl-phenyl-propyl-alkine.* (262°). Colourless liquid. Insoluble in water. Very weak base. Formed by heating ethyl-aniline with propylene-chlorhydrin (Laun, *B.* 17, 678).

DI-ETHYL-OXY-PROPYLENE-DIAMINE $CH_2(OH).CH(NHEt).CH_2(NHEt)$. (c. 185°). From epichlorhydrin and ethylamine (Reboul, *C. R.* 97, 1488). Syrup, miscible with water.

Tetra-ethyl-oxy-propylene-di-amine $N_2HEt_4.C_3H_4OH$ *i.e.* $CH_2(OH).CH(NEt_2).CH_2.NEt_2$.

According to Behrend (*B.* 17, 511) this base, obtained from diethylamine and the dichloride of allyl alcohol, is a liquid which cannot be distilled, but which forms an aurochloride $B'(HAuCl_4)_2$ that crystallises in plates, sl. sol. water, and also a *benzoyl derivative* $CH_2(OBz).CH(NEt_2).CH_2NEt_2$, of which the platino-chloride $B''H_2PtCl_4$ forms orange-red needles.

Tetra-ethyl-oxy-propylene-diamine $(C_3H_5.OH)(C_2H_5)_4N_2$ *i.e.* $CH_2(NEt_2).CH(OH).CH_2(NEt_2)$. *Tetra-ethyl-allyl-alkine.* (235°). S.G. $\frac{4}{4}$ ·9002. Colourless liquid, lighter than, and slightly soluble in, water. Formed by heating *s*-dichlorhydrin with diethylamine, or by mixing epichlorhydrin with diethylamine. The platino-chloride $B''H_2PtCl_6$ forms long thick soluble prisms; the aurochloride forms fine needles (Berend, *B.* 17, 510; Reboul, *C. R.* 97, 1488).

Benzoyl derivative $CH(OBz)(CH_2NEt_2)_2$. Gives an orange platino-chloride $B''H_2PtCl_6$.

ETHYL OXYSULPHIDE *v.* ETHYL SULPHOXIDE.

o-**ETHYL-PHENOL** [4:1]$C_6H_4Et(OH)$. *Phlorol.* Mol. w. 122. (211°) (O.); (220°) (C.).

Formation.—1. From *o*-amido-phenyl-ethane by the diazo- reaction (Suida a. Plohn, *Sitz. W.* [2] 81, 245; *M.* 1, 175). When the amido-phenyl-ethane used is obtained by reducing the crude product of the nitration of ethyl-benzene the *o*-ethyl-phenol constitutes three-fourths of the resulting product.—2. By distilling barium phloretate with lime; phenol being also formed (V. Oliveri, *G.* 13, 263).—3. By fusing ethyl-benzene (*β*)-sulphonic acid with potash.—4. From its methyl ether.—5. By distilling gum ammoniac (1 pt.) with zinc-dust (10 pts.) (Ciamician, *B.* 12, 1658).

Properties.—Colourless liquid smelling like phenol. Liquid at −18°. Sl. sol. water, v. sol. alcohol and ether. Gives a greenish colouration with ferric salts. Dissolves in alkalis. Yields salicylic acid and a small quantity of *m*-oxy-benzoic acid when fused with potash. Reacts with conc. HNO_3 with explosive violence.

Salt.—$Ba(O.C_6H_4Et)_2$ 2aq: leaflets, decomposing at 100°.

Methyl ether $C_6H_4Et.OMe$. (185°) (O.); (191°) (S. a. P.). Heavy oil of pleasant ethereal odour. Not attacked by chromic acid mixture or by $KMnO_4$.

(*α*)-**Ethyl-phenol** $C_6H_4Et(OH)$. [47°]. (215°). Formed by fusing ethyl-benzene (*α*)-sulphonic acid with potash (Beilstein a. Kuhlberg, *A.* 156, 211; Fittig a. Kiesoff, *A.* 156, 251). Needles. Sl. sol. water, v. e. sol. alcohol and ether. Its aqueous solution is coloured greenish-blue by Fe_2Cl_6. When heated with P_2O_5 it gives phenyl phosphate and ethylene (Chrustschoff, *B.* 7, 1165). Conc. HNO_3 gives CO_2 and oxalic acid.

Ethyl-phenol $C_6H_4Et.OH$. (204°–215°) (E.). S.G. ^{14} 1·049 (A.). Prepared by heating a mixture of phenol and ethyl alcohol with zinc-chloride (Auer, *B.* 17, 669). A mixture of ethyl-phenols is formed by this process (Errera, *G.* 14, 484). Its aqueous solution is coloured greenish by ferric chloride.

Ethyl ether $C_6H_4Et(OEt)$. (200°) (E.). Oxidised by $KMnO_4$ to *p*-oxy-benzoic ether.

Acetyl derivative $C_6H_4Et(OAc)$. (c. 225°).

Di-ethyl-phenol $C_6H_3Et_2(OH)$ [1:3:4?]. (225°). From *m*-di-ethyl-benzene. Gives a bluish-violet colour with $FeCl_3$.

Reference.—DI-BROMO-ETHYL-PHENOL.

ETHYL-PHENOL CARBOXYLIC ACID *v.* OXY-ETHYL-BENZOIC ACID.

ETHYL-PHENOL-PHTHALEÏN $C_{22}H_{18}O_4$. Formed by heating ethyl-phenol with phthalic anhydride and $ZnCl_2$ (Auer, *B.* 17, 671). Grey crystalline powder (containing aq). V. sol. alcohol and ether, insol. water. Dissolves in alkalis forming a violet solution.

o-**ETHYL-PHENOL SULPHONIC ACID** $C_6H_3Et(OH)SO_3H$. From *o*-ethyl-phenol and conc. H_2SO_4 (Suida a. Plohn, *Sitz. W.* [2] 81, 245; *M.* 1, 179). Very deliquescent minute needles.—$BaA'_2\,x$aq : pearly plates. Its solution gives a white pp. with lead salts and a dirty-green pp. with copper salts.

(*a*)-Ethyl-phenol sulphonic acid $C_6H_3Et(OH).SO_3H$. From (*a*)-ethyl-phenol and conc. H_2SO_4 (Fittig a. Kiesoff, *A.* 156, 254).—BaA'_2 : prisms. S. 4·7 at 17° (Baumann, *H.* 4, 313).—$BaC_8H_8O_4$: insol. water.

ETHYL-DIPHENYL $C_6H_5.C_6H_4(C_2H_5)$. [1:3]. (284°). S.G. $^{\underline{0}}$ 1·043. Formed by treating melted diphenyl and $AlCl_3$ with C_2H_5Cl, C_2H_5Br, or with C_2H_4. The C_2H_5Br gives the best yield (Adam, *A. Ch.* [6] 15, 251; *Bl.* [2] 47, 689). Colourless, mobile liquid. Oxidised with chromic acid it gives $C_6H_5.C_6H_4.CO_2H$ [1:3] [161°]. Traces of $C_6H_5.C_6H_4.COCH_3$ can be obtained as an intermediate product. Bromine at 180° easily produces a dibromide $C_{14}H_{12}Br_2$. [103°]. Insol. alcohol and ether.

Di-ethyl-diphenyl $C_6H_5.C_6H_3(C_2H_5)_2$. S.G. $^{\underline{0}}$ ·999. (c. 307°). Formed by treating melted diphenyl and $AlCl_3$ with C_2H_4, C_2H_5Cl, or C_2H_5Br, the latter giving the best yield (Adam). A colourless liquid. When oxidised with chromic acid (1,3,5) diphenyl-di-carboxylic acid is obtained.

Reference.—DI-AMIDO-DI-ETHYL-DIPHENYL.

ETHYL-PHENYL- *v.* PHENYL-ETHYL-.

ETHYL-PHENYL-ACETIC ALDEHYDE $C_6H_4Et.CH_2.CHO$. From di-ethyl-benzene by successive treatment with CrO_2Cl_2 and water (Etard, *A. Ch.* [5] 22, 255). Liquid. Volatile with steam. Decomposed by heating to 220°. Combines with $NaHSO_3$.

ETHYL-PHENYL-AMIDO-NAPHTHOQUINONE *v.* NAPHTHOQUINONE-ETHYL-ANILIDE.

ETHYL-PHENYL-AMINE *v.* AMIDO-PHENYL-ETHANE.

TRI-ETHYL-PHENYL-AMMONIUM HYDROXIDE *v.* *Ethylo-hydroxide* of DI-ETHYL-ANILINE.

TRI-ETHYL-PHENYL-ARSONIUM compounds *v.* ARSENIC, *Organic compounds of.*

ETHYL-PHENYL BENZYL KETONE *v.* BENZYL ETHYL-PHENYL KETONE.

p-**ETHYL-PHENYL-*p*-ISOBUTYL-PHENYL-THIO-UREA** $C_4H_9.C_6H_4.NH.SCNH.C_6H_4(C_2H_5)$. *Phenethyl-phenisobutyl-thiourea.* [140°]. Formed from *p*-ethyl-phenyl thiocarbimide and *p*-butyl-phenyl-amine (Mainzer, *B.* 16, 2025). Small white prisms. Sol. hot alcohol. By phosphoric acid it is split up into *p*-isobutyl-phenyl thiocarbimide *p*-ethyl-phenyl thiocarbimide, *p*-isobutyl-phenyl-amine, and *p*-ethyl-phenyl-amine.

ETHYL-PHENYLENE-DIAMINE *v.* PHENYLENE-ETHYL-DIAMINE.

ETHYL-DI-PHENYL-ETHANE *v.* PHENYL-ETHYLPHENYL-ETHANE.

ETHYL-DI-PHENYL-ETHYLENE $C_6H_5.CH:CH.C_6H_4Et$. [90°]. Formed from $Ph.CH_2.CH(OH).C_6H_4Et$ and boiling dilute H_2SO_4 (Söllscher, *B.* 15, 1681). Plates, v. e. sol. ether.

Di-ethyl-di-phenyl-ethylene $C_6H_4Et.CH:CH.C_6H_4Et$. *Di-ethyl-stilbene.* [135°]. Obtained by distilling the product of the action of H_2SO_4 on a mixture of ethyl-benzene and $Et.O.CHCl.CH_2Cl$ (Hepp, *B.* 7, 1414). Pearly plates (from alcohol); sl. sol. cold alcohol, v. sol. ether. Boiling dilute HNO_3 oxidises it to terephthalic acid. It combines with Br.

DI-*p*-ETHYL-PHENYL-GUANIDINE $HN:C(NH.C_6H_4Et)_2$. *Di-p-phenethyl-guanidine.* [138°]. Formed by the action of alcoholic NH_3 and lead oxide upon di-*p*-ethyl-phenyl-thio-urea (Paucksch, *B.* 17, 2804). Large transparent tables. V. sol. alcohol, ether, and CS_2. —$B''H_2Cl_2PtCl_4$: glistening plates.

ETHYL-DI-PHENYL-KETONE *v.* PHENYL-ETHYL-PHENYL-KETONE.

DI-ETHYL-PHENYL-METHANE *v.* AMYL-BENZENE.

p-**ETHYL-PHENYL-(*a*)-NAPHTHYL-THIO-UREA** $C_{10}H_7NH.CS.NH.C_6H_4Et$. *Phenethyl-(a)-naphthyl-thiourea.* [148°]. Prepared by mixing (*a*)-naphthyl thiocarbimide and ethyl-phenyl-amine in alcoholic solution (Mainzer, *B.* 16, 2022). Small white needles. Sol. hot alcohol and ether. By phosphoric acid it is split up into *p*-ethyl-phenyl-thiocarbimide, (*a*)-naphthyl-thiocarbimide, *p*-ethyl-phenyl-amine, and (*a*)-naphthylamine.

p-**Ethyl-phenyl-(*β*)-naphthyl-thio-urea** $C_{10}H_7NH.CS.NHC_6H_4Et$. [159°]. Prepared as above, using (*β*)-naphthyl-thiocarbimide ((*β*)-naphthyl mustard-oil) (M.). Small plates (from alcohol). M. sol. hot alcohol and ether. Split up like the (*a*)-isomeride by phosphoric acid.

DI-*a*-ETHYL-DI-PHENYL-PROPIONIC ACID $C_{19}H_{22}O_2$ *i.e.* $(C_6H_4.C_2H_5)_2:C(CH_3).CO_2H$. [116°]. Prepared by dissolving ethyl-benzene and pyruvic acid in H_2SO_4 (Böttinger, *B.* 14, 1597). Transparent tables. Sol. ether, chloroform, and ligroïn.

ETHYL-PHENYL-PROPYL-ALKINE *v.* ETHYL-OXYPROPYL-ANILINE.

ETHYL PHENYL SULPHONE *v.* PHENYL ETHYL SULPHONE.

ETHYL-PHENYL DI-SULPHOXIDE *v.* BENZENE THIOSULPHONIC ACID.

ETHYL-PHENYL-THIOBIURET *v.* *Ethyl-derivative* of PHENYL-THIOBIURET.

o-**ETHYL-PHENYL THIOCARBIMIDE** $C_6H_4(C_2H_5).NCS$. (240°–245°). *o-Phenethyl-mustard oil.* Colourless mobile liquid. Formed by heating the thio-urea with phosphoric acid (Paucksch, *B.* 17, 2802).

p-**Ethyl-phenyl thiocarbimide** $SCN.C_6H_4(C_2H_5)$. *Phenethyl mustard oil.* (256°).

Liquid. Formed by distilling di-*p*-ethyl-phenyl-thiourea with phosphoric acid (Mainzer, *B.* 16, 2020).

DI-*o*-ETHYLPHENYL-THIO-UREA $C_{17}H_{20}N_2S$ *i.e.* $SC(NH.C_6H_4Et)_2$. [142°]. White needles. Obtained by heating *o*-amido-ethyl-benzene with CS_2 and a little NaOH (Paucksch, *B.* 17, 767).

Di-*p*-ethylphenyl-thio-urea $C_{17}H_{20}N_2S$ *i.e.* $SC(NH.C_6H_4Et)_2$. [145°]. Obtained by heating *p*-amido-ethyl-benzene with CS_2 and a little NaOH (Paucksch, *B.* 17, 768; *cf.* Mainzer, *B.* 16, 2019). Pearly plates. Soluble in hot, sparingly in cold, alcohol.

ETHYL-PHENYL-TOLUENE *v.* BENZYL-ETHYL-BENZENE.

DI-*p*-ETHYL-PHENYL-UREA $OC(NH.C_6H_4Et)_2$. *Di-p-phen-ethyl-urea.* [217°]. Long transparent needles. Formed by the action of carbonyl chloride ($COCl_2$) upon *p*-ethyl-phenyl-amine (Paucksch, *B.* 17, 2804).

PENTA-ETHYL-PHLOROGLUCIN $C_6Et_5O_3H$ *i.e.* $C_6EtO_2(Et_2)_2(OH)$. [92°]?

Preparation.—Phloroglucin (1 mol.) is warmed with KHO (3 mols.) and EtI (3 mols.) in alcoholic solution. The alcohol is finally distilled off and the residue dissolved with water and extracted with ether.

Properties.—Yellow indifferent body; when repeatedly crystallised from weak alcohol, it forms white plates. It is not acted on by boiling HIAq. It reacts with more EtI and KHO, showing that it still contains a HO group, forming an oil $C_{18}H_{30}O_3$ or hexa-ethyl-phloroglucin $C_6O_3Et_6$ (Herzig a. Zeisel, *M.* 9, 217).

ETHYL PHOSPHATES

Mono-ethylortho-phosphate $C_2H_5O.PO(OH)_2$. *Ethyl-phosphoric acid.* Formed by the action of phosphoric acid on alcohol or ether (Lassaigne, *A. Ch.* [2] 13, 294; Pelouze, *A. Ch.* [2] 52, 37; Liebig, *A.* 6, 149; 13, 32; Church, *Pr.* 13, 520; Vogeli, *P.* 74, 282). A mixture of alcohol (1 pt. of 95 p.c.) with syrupy ortho- or pyro-phosphoric acid (1 pt.) is heated for some minutes to 70°, left to stand for 24 hours, and then diluted with water and neutralised with $BaCO_3$. The Ba salt is crystallised and decomposed by H_2SO_4.

Properties.—Colourless viscid liquid miscible with water, alcohol, and ether. It reddens litmus and tastes sour. It gives off ether, alcohol, and ethylene when heated. Distilled with KOAc it yields acetic ether.

Salts.—Soluble in water and crystalline. Most of them have a maximum degree of solubility at 40° to 60°. The lead salt is the least soluble: $As_2A''_3$: feathery crystals (Church).—BaA'' 6aq: prisms or tables. S. 3·4 at 0°; 6·72 at 20°; 9·36 at 40°; 2·80 at 100°.—BaA''aq (C.).—BaA'' 7aq (C.).—CaA'' 2aq: micaceous scales.—$Fe_2A''_3$ 3aq: straw-yellow films (C.).—$Fe_2AlA''_6$ 6aq (Church).—$FeAlA''_3$ 3aq (C.).—$FeAl_3A''_6$ 6aq (Church).—$Fe_5A''_6$ 6aq (Church).—PbA''aq.—Hg_2A'' 2aq (?) (Church).—UrO_2A': lemon-yellow mass.—AgA'aq: crystalline.—Tetra-ethyl-ammonium salt $(NEt_4)_2A''$: deliquescent mass of crystals; split up by heat into triethylamine and tri-ethyl phosphate.

Chloride $EtO.OPCl_2$. (167°). Formed by the action of alcohol (1 mol.) on $POCl_3$ (1 mol.) or by passing chlorine into a mixture of alcohol (2 mols.) and PCl_3 (1 mol.) (Wichelhaus, *A. Suppl.* 6, 265). Formed also by heating Et_3PO_4 with $POCl_3$ at 110° (Chambon, *J.* 1876, 205). Oil; split up at 160° into EtCl, $POCl_3$ and P_2O_5, but may be distilled in a current of hydrogen. Decomposed by water into HCl and $EtO.OP(OH)_2$. PBr_5 gives EtBr, $POBr_3$, and $POBrCl_2$.

Di-ethyl phosphate $(EtO)_2PO.OH$. *Di-ethyl-phosphoric acid.* Prepared by placing P_2O_5 in a dish over dry ether, or, better, alcohol under a bell-jar. In a fortnight the acid will have deliquesced, and the syrup may then be treated with $PbCO_3$. The resulting lead salt is decomposed by H_2S (Vögeli, *A.* 69, 180). Syrup; decomposed by heat.—CaA'_2: silky groups of crystals (from water); v. sol. water, sl. sol. alcohol; gives off Et_3PO_4 when heated.—PbA'_2: [180°]; groups of crystals resembling caffeine (from water); v. sol. cold water and hot alcohol. At 190° it gives off Et_3PO_4 leaving $PbEtPO_4$.—The barium salt forms needles or laminæ, v. sol. water.

Chloride $(EtO)_2OPCl$. From $POCl_3$ (1 mol.) and alcohol (2 mols.) also from Et_3PO_4 and Cl (W.).

Bromide $(EtO)_2OPBr$. From Et_3PO_4 and Br (W.). Cannot be distilled.

Tri-ethyl phosphate Et_3PO_4 *i.e.* $OP(OEt)_3$. *Phosphoric ether.* (215°). S.G. $^{\underline{12}}$ 1·072.

Formation.—1. By heating $Pb(Et_2PO_4)_2$ to 190° (*v. supra*).—2. In small quantity in the preparation of di-ethyl phosphate (V.).—3. By heating Ag_3PO_4 with AgI at 100°, exhausting the mass with ether, and distilling *in vacuo* (De Clermont, *A.* 91, 376).—4. From $POCl_3$ and NaOEt (Limpricht, *A.* 134, 347).—5. By treating dry alcohol with $POCl_3$ or P_2O_5 (Schiff; Carius, *A.* 137, 121).

Properties.—Limpid liquid with peculiar odour. In a current of hydrogen it boils at 203°. Sol. water, alcohol and ether. Slowly decomposed by contact with water forming HEt_2PO_4. $POCl_3$ at 110° forms $EtO.POCl_2$. When PCl_3 (1 pt.) mixed with pure ether is dropped upon dry NaOEt (6 pts.) suspended in ether and the product distilled in a current of hydrogen there is obtained a compound (158° cor.). S.G. $^{\underline{14}}$ ·960 which may be $C_{14}H_{36}P_2O_8$ or $(Et_3PO_4)(Et_3PO_3)(EtOH)$; it is slowly split up by distillation into its components (Geuther, *A.* 224, 275).

Ethyl metaphosphate $EtPO_3$? (below 100°). From lead metaphosphate and EtI (Carius, *J.* 1861, 586). Water converts it into EtH_2PO_4.

Tetra-ethyl pyrophosphate $Et_4P_2O_7$. S.G. $^{\underline{17}}$ 1·172. From silver pyrophosphate by heating at 100° with EtI (De Clermont, *A.* 91, 375). Viscid liquid with peculiar odour and burning taste. Decomposed by heat. Burns with whitish flame. Sol. water, alcohol, and ether. It turns acid when exposed to the air. Potash forms KEt_2PO_4.

ETHYL-PHOSPHINE C_2H_7P *i.e.* PH_2Et. Mol. w. 62. (25°). When EtI and PH_4I are heated together with ZnO at 150° there is formed $PEtH_3I$ and PEt_2H_2I. On treating the product with water $PEtH_3I$ is decomposed into HI and gaseous $PEtH_2$ while PEt_2H_2I is not affected. If after expelling $PEtH_2$ aqueous NaOH be now added it will liberate PEt_2H (Hofmann, *B.* 4, 432). PH_2Et is also formed when ethylene bromide, PH_4I, and ZnO are heated together (Hofmann, *B.* 6, 302). Very volatile liquid. It has no action on litmus. Has an overpowering odour; its vapour produces an intensely bitter taste in the throat. It bleaches cork. Takes fire with Cl, Br, or fuming HNO_3. Combines with S and CS_2 forming liquid bodies.

Salt.—$PEtH_2I$: four-sided tables, decomposed by water, partially decomposed by alcohol; insol. ether. It is ppd. in crystalline form by adding ether to its solution in conc. HIAq.

Ethyl-di-chloro-phosphine $EtPCl_2$. *Ethyl-phosphorous chloride.* (110°). Formed by heating PCl_3 (4 pts.) with mercuric ethide $HgEt_2$ (1 pt.) (Michaelis, *B.* 18, 2174). Liquid smelling like apples. Fumes in the air. Is readily decomposed by water. With Cl it gives $EtPCl_4$ a solid which decomposes at 100°-150° and is converted by water into $EtPOCl_2$, a liquid boiling about 175°, which is decomposed by further treatment with water.

Di-ethyl-phosphine Et_2PH. Mol. w. 90. (85°). Is prepared as above (Hofmann, *B.* 4, 433). Oil with powerful odour; lighter than water. Absorbs oxygen from the air, sometimes taking fire. Combines directly with sulphur and with CS_2 forming liquid compounds. Its salts crystallise with difficulty.

Tri-ethyl-phosphine PEt_3. Mol. w. 118. (128°). S.G. $^{\underline{15}}$ ·812.

Formation.—1. By the action of PCl_3 on $ZnEt_2$ (Hofmann a. Cahours, *C. J.* 11, 56; *A.* 104, 1; *Suppl.* 1, 2). The tri-ethyl-phosphine remains combined with $ZnCl_2$ but may be liberated by distillation with aqueous potash.—2. By the action of phosphide of sodium on EtI (Berlé, *J. pr.* 66, 78).—3. When a mixture of zinc, phosphorus, and dry EtI is heated at 155° there is produced, together with $ZnEt_2$, a mixture of $(PEt_3HI)_2ZnI_2$ with $(PEt_4I)_2ZnI_2$ and $(PEt_3O)_2ZnI_2$. These compounds may be separated by water, the first being the least and the second the most soluble. The first yields PEt_3 when treated with cold potash, the third yields it when heated with solid KOH (Hofmann, *C. J.* 13, 291).—4. When zinc phosphide obtained by passing dry PH_3 into a well-cooled ethereal solution of $ZnEt_2$ is heated with (5 pts. of) EtI at 150° it forms $(Et_3PHI)_2ZnI_2$ (Drechsel a. Finkelstein, *B.* 4, 352).

Preparation.—1. PCl_3 is allowed to drop slowly into an ethereal solution of $ZnEt_2$ placed in a retort filled with CO_2 connected with a tubulated receiver. The reaction is violent, and, to avoid loss, the other tubulure of the receiver is connected with a V tube containing PCl_3 communicating with a vessel full of CO_2. The liquid separates into two layers, the lower being the zinc double salt of PEt_3; this salt is distilled with aqueous KOH in a current of hydrogen. It is dried with solid KOH and rectified in hydrogen (Hofmann, *C. J.* 13, 290).—2. PH_4I (1 mol.) is heated with alcohol (3 mols.) for 8 hours at 180°. The product containing PEt_3HI and PEt_4I is distilled with potash (Hofmann, *B.* 4, 207).

Properties.—Colourless, mobile, liquid. Its odour is very penetrating but not disagreeable; when diluted it smells like hyacinths. When freshly prepared it has no action on litmus, but if exposed for a few seconds to the air it becomes acid. It is insol. water, miscible with alcohol and ether. It unites with acids forming very deliquescent salts.

Reactions.—1. Rapidly absorbs *oxygen* from the air, becoming PEt_3O. It often takes fire in pure oxygen, forming P_2O_5. Its vapour mixed with oxygen explodes when heated.—2. *Sulphur* combines with it forming PEt_3S.—3. *Selenium* gives PEt_3Se.—4. *Sulphide of carbon* unites with it forming red monoclinic crystals of PEt_3CS_2 [95°]. Hence CS_2 and PEt_3 may be used to detect one another; thus, when the vapour of CS_2 is poured over a watch glass in which there is a liquid containing free PEt_3, a beautiful net-work of the red crystals will appear. The crystals are insol. water, sl. sol. ether, m. sol. warm alcohol and CS_2. They dissolve in conc. HClAq, forming a colourless solution from which they are re-ppd. by KOH unaltered. Water at 100° gives PEt_3S, PEt_3O, and $PMeEt_3OH$. Boiling with alcohol and Ag_2O forms PEt_3S and CO_2. H_2S also gives PEt_3S and yellow crystals of $C_8H_{17}PS_3$, which are converted by hot water into CS_2 and $C_7H_{19}PSO$, whence $C_7H_{18}PSI$ may be prepared. Platinic chloride forms the compound $(PEt_3CS_2)_2H_2PtCl_6$ an amorphous light yellow salt.—5. When PEt_3 is poured into a flask containing *chlorine* every drop takes fire, PCl_5, HCl, and carbon being formed. If the reaction be moderated a crystalline compound PEt_3Cl_2 is formed. This melts near 100°, but has a very high boiling-point. *Bromine* and *iodine* act in the same way.—6. *Ethylene bromide* forms $CH_2Br.CH_2.PEt_3Br$ and $C_2H_4(PEt_3Br)_2$. *Ethylidene bromide*, ethylidene chloride, and EtCl act in like manner. *Ethylene iodide*, however, acts with explosive violence, forming PEt_3I_2 and ethylene. — 7. *Chloro-acetic ether* forms $PEt_3Cl.CH_2.CO_2Et$ (Hofmann, *Pr.* 11, 525).—8. *Allyl thiocarbimide* (oil of mustard) forms $C_3H_5NCSPEt_3$ possibly $C_3H_5NEt.CS.PEt_2$. It forms large crystals (from ether) [68°] and gives with H_2PtCl_6 the salt $B'_2H_2PtCl_6$ (Hofmann, *Tr.* 1860, 440).—9. *Phenyl-thio-carbimide* forms in like manner 'phenyl-tri-ethyl-phospho-thio-urea' $CS(NPhEt)(PEt_2)$ [58°] (Hofmann, *Tr.* 1860, 432). It forms monoclinic crystals (from ether), isomorphous with $CS(NC_3H_5Et)(PEt_2)$ and with allyl thio-urea. It decomposes at 100°. It is insol. water, sol. alcohol and boiling ether. It is very soluble in dilute acids, forms easily crystallisable salts. HNO_3 forms phenyl thiocarbimide and PEt_3O. Boiling aqueous NH_3 forms phenyl-thio-urea and PEt_3. KOH gives PEt_3, di-phenyl-thio-urea, K_2S, and K_2CO_3. CS_2 forms the red PEt_3CS_2. Phenyl-tri-ethyl-phospho-thio-urea forms the following combinations: B'HCl. cadmium yellow crystals, decomposed by boiling water.—$B'_2H_2PtCl_6$.—B'MeI: golden needles (from boiling water). — $(B'MeCl)_2PtCl_4$. — B'MeOH: decomposed on boiling into PhNCS and PEt_3MeOH.—10. *Ethyl sulphocyanide* forms PEt_3S and PEt_4Cy.—11. Tri-ethyl-phosphine merely polymerises *cyanic acid* and its ethers.—12. *Mercaptan* even at 100° has no action unless air be present.—13. *Iodoform* reacts with rise of temperature, producing $CH(PEt_3)_3I_3$ which crystallises from alcohol. It is v. sol. water, sl. sol. alcohol, insol. ether. Aqueous ZnI_2 gives in its solution a pp. of $\{CH(PEt_3)_3I_3\}_2 3ZnI_2$. Platinic chloride gives $\{CH(PEt_3)_3Cl_3\}_2PtCl_4$, which crystallises from alcohol in rectangular laminæ.

Moist Ag_2O forms $PEt_3Me(OH)$ and PEt_3O (Hofmann, *Pr.* 10, 189; 11, 290).—14. *Chloroform* or CCl_4 give $CH(PEt_3)_3Cl_3$.—15. By dropping PEt_3 upon cooled *chloro-acetic acid* in a vessel full of hydrogen there is formed $Et_3PCl.CH_2.CO_2H$ 'the hydrochloride of phosphorus betaïne' (Letts, *Tr. E.* 30, 285; *Pr. E.* 11, 40). This compound crystallises from ether in colourless needles, it has an acid reaction, and its platinochloride forms thick light orange needles. The compound $Et_3PCl.CH_2.CO_2H$ splits up at 145° into CO_2 and PEt_3MeCl. Solid KOH gives PEt_3O and potassium acetate. Moist Ag_2O forms $Et_3P(OH).CH_2.CO_2H$ which, when dried over P_2O_5 *in vacuo*, becomes $Et_3P<\genfrac{}{}{0pt}{}{O—}{CH_2}>CO$, a very deliquescent neutral substance. HBr converts it into $Et_3PBr.CH_2.CO_2H$, which forms dimetric plates (from alcohol and ether). It is split up by heat into CO_2 and PEt_3MeBr. HI converts $Et_3P(OH).CH_2.CO_2H$ into very deliquescent granular crystals of the acid $Et_3PI.CH_2.CO_2H$. $PEt_3Cl.CH_2.CO_2H$ is converted by Ag_2SO_4 into a very deliquescent sulphate which is split up by heat into CO_2 and $(PEt_3Me)_2SO_4$.—16. PEt_3 mixed with an equimolecular quantity of cooled *chloro-acetic ether* forms very deliquescent $PEt_3Cl.CH_2.CO_2Et$ which melts below 100°, and at a higher temperature is split up into PEt_3MeCl, CO_2, and ethylene. It forms a crystalline platinochloride, and is converted by moist Ag_2O into $Et_3P<\genfrac{}{}{0pt}{}{O—}{CH_2}>O$, alcohol, PEt_3O, and acetic ether. Solid KOH forms PEt_3O, acetic ether, and KCl (Letts, *Tr. E.* 30, 285).—17. *Bromo-acetic ether* forms in like manner an extremely deliquescent compound which melts below 100°, and is split up by heat into PEt_3MeBr, CO_2, and ethylene (Letts).—18. *Bromo-acetic acid* forms a colourless liquid which if heated to 100° and allowed to cool solidifies. The product consists of at least two substances: one of these substances, ($PEt_3Br.O.CO.CH_3$?), when treated with potash yields PEt_3O and KOAc; the other, which is perhaps $PEt_3H.O.CO.CH_2Br$, yields PEt_3 with KOH. The first compound is also formed when PEt_3O is treated with acetyl bromide (Letts, *Tr. E.* 30, 285).

Salts.—The hydrochloride, hydrobromide, hydroiodide, sulphate, and nitrate are crystalline but extremely deliquescent.—$(PEt_3HI)_2ZnI_2$: tablets.—$(PEt_3)_2H_2PtCl_6$: crystalline, sl. sol. cold water, insol. alcohol and ether. By boiling PEt_3 with aqueous platinic chloride there are formed two isomeric compounds of the formula $(PEt_3)_2PtCl_2$, a white substance insol. ether, and a yellow substance crystallising from ether in prisms [150°]. The yellow substance is insol. water, and is converted into its isomeride by heating with alcohol at 100°. When boiled with water and PEt_3 it forms $(PEt_3)_4PtCl_2$ (Cahours a. Gal, *Z.* 1870, 350, 437).—$(PEt_3)_2PdCl_2$.—$(PEt_3)_4Pt_2Cl_6$.—$(PEt_3)_4PtCl_2Au_2Cl_6$.—$(PEt_3)_2AuCl$.

Tri-ethyl-phosphine oxide PEt_3O. Mol. w. 134. [44°] (H.); [53°] (P.). (243° uncor.). V.D. 4·60 (calc. 4·66).

Formation.—1. From PEt_3 by atmospheric oxidation or by gently heating it with HgO or Ag_2O (Cahours a. Hofmann, *A.* 104, 18).—2. By distilling PEt_4OH, the other product being ethane.—3. By decomposing $(PEt_4Cl)_2ZnCl_2$ with solid KOH and a little water (Pebal, *A.* 120, 194).—4. From $EtOPCl_2$ and $ZnEt_2$ (Wichelhaus, *B.* 1, 80).—5. By heating clear phosphorus (1 pt.) with EtI (13 pts.) for 24 hours at 180°, and boiling the product with alcohol. The residue is evaporated and distilled with KOH (4 pts.) (Crafts a. Silva, *Z.* 1871, 359; *cf.* Carius, *A.* 136, 137). When PI_3 (1 mol.) is heated with EtI (3 mols.) iodine is given off, and a body is left which when treated with solid KOH yields PEt_3O on distillation (Emmerton, *Am.* 4, 9).

Properties. — Slender white deliquescent needles. Dissolves in all proportions in water and alcohol, less sol. ether. Very slightly volatile with steam. Separates as a liquid when solid KOH is added to its aqueous solution, or when ether is added to its alcoholic solution. Converted by HBr into PEt_3Br_2, and by HI into PEt_3I_2. It is not affected by H_2S or by halogens. It forms crystalline compounds with some metallic salts: $(PEt_3O)_3CuSO_4$: deliquescent, four-sided, green prisms (Pebal).—$(PEt_3O)_2ZnI_2$: [99°]; crystalline pp. which, when crystallised from alcohol, forms monoclinic crystals; *a*:*b*:*c* = ·905:1:·331; β = 83° 13′.

Tri-ethyl-phosphine oxy-chloride $(PEt_3)_2OCl_2$. By passing dry HCl over fused PEt_3O shining crystals are formed, which are dissolved in HClAq and the solution is then evaporated (Hofmann). Very deliquescent crystalline mass, sol. water and alcohol, insol. ether. The solution treated with platinic chloride in saturated alcoholic solution yields $(P_2Et_6O_2Cl_4)_3PtCl_4$, which crystallises from alcohol in large orange monoclinic prisms; *a*:*b*:*c* = ·631:1:1·578; β = 73° 42′ (Hofmann, *Tr.* 1860, 419).—$(PEt_3)_2OCl_2ZnCl_2$: transparent octahedra, sol. water and alcohol. By the action of HCl on PEt_3O Crafts a. Silva obtained a compound $PEt_3(OH)Cl$ [128°].

Tri-ethyl-phosphine sulphide PEt_3S. [94°].

Formation.—1. By adding flowers of sulphur to an ethereal solution of PEt_3; after evaporating the ether the residue is heated with boiling water which dissolves PEt_3S only, depositing it in crystals on cooling.—2. By distilling PEt_3 with cinnabar.—4. By decomposing PEt_3CS_2 with water or Ag_2O.—5. By the action of mercaptan on PEt_3 in presence of air.

Properties.—Long hexagonal needles (from water); *a*:*c* = 1: ·821. Sol. water, v. sol. alcohol and ether, v. e. sol. CS_2. Volatile with steam. Decomposed by sodium giving Na_2S and PEt_3. It may be separated from its aqueous solution by KOH. Its aqueous solution is neutral to litmus, but it dissolves more readily in HClAq than in water, and the solution gives an unstable yellow pp. with platinic chloride. The aqueous solution is not affected by boiling aqueous lead acetate or $AgNO_3$ or by HgO, but these substances become sulphides when added to its alcoholic solution.

Tri-ethyl-phosphine selenide PEt_3Se. [112°]. From PEt_3 and selenium. Crystallises from water, but turns red in air.

Tetra-ethyl-phosphonium compounds.

$PEt_4(OH)$. When PEt_4I is digested with water and Ag_2O there is formed a strongly alkaline bitter solution, which dries up over H_2SO_4 to an extremely deliquescent crystalline mass. This solid hydroxide absorbs CO_2 with avidity. Its solution behaves like KOH towards solutions of metallic salts; alumina and zinc hydrate, however, dissolve less readily in excess of PEt_4OH than in KOHAq. PEt_4OH is split up by heat into PEt_3O and ethane.—$(PEt_4)_2SO_4$: split up by heat into PEt_3S, PEt_3O, and charred products. Chlorine at 130° forms $(PEt_4)_2SO_4Cl_4$, a yellow body (Masson a. Kirkland, *C. J.* 55, 133). Bromine vapour at 110° gives $(PEt_4)_2SO_4Br_{12}$ and $(PEt_4)_2SO_4Br_2$.—$(PEt_4)_2CO_3$: resolved by heat into PEt_3, PEt_3O, di-ethyl-ketone, C_4H_{10}, and CO_2.—PEt_4Cl: deliquescent. Resolved by heat into C_2H_4 and PEt_3HCl (Letts a. Collie, *C. J. Proc.* 2, 164).—PEt_4Cl_3: deliquescent; decomposed by water, forming PEt_3Cl (Masson a. Kirkland, *C. J.* 55, 132).—PEt_4AuCl_4: yellow needles (from water).—$(PEt_4Cl)_2PtCl_4$: regular octahedra (from water); sl. sol. boiling water, insol. alcohol and ether.—$(PEt_4Cl)_3 2BiCl_3$: six-sided tables (Jörgensen, *J. pr.* [2] 3, 345).—$(PEt_4Cl)_2ZnCl_2$: from $ZnEt_2$ by gradual addition of $POCl_3$ followed by water (Pebal, *A.* 120, 198); colourless dimetric crystals, permanent in the air and v. sol. water.—$(PEt_4Br)_3 2BiBr_3$ (J.).—PEt_4Br_3: formed by evaporating an alcoholic solution of the following salt. Red crystals.—PEt_4Br_7: from PEt_4Br and bromine vapour at 110°. Violet crystals (M. a. K.).—PEt_4ICl_2.—PEt_4IBr_4.—PEt_4IBr_2.—PEt_4I: formed with great violence when PEt_3 and EtI are mixed. Rhombohedra, isomorphous with AgI. V. sol. water, m. sol. alcohol, insol. ether. The aqueous solution crystallises on addition of KOHAq in which it is but slightly soluble. It is not decomposed by KOHAq.—$(PEt_4I)_2ZnI_2$: crystals; formed by heating crystallised phosphide of zinc with EtI at 175° (Cahours, *A.* 112, 228; 122, 192).—PEt_4I_3: [67°]; brown plates (Jörgensen, *Z.* 1871, 770).—PEt_4ITlI_3 (Jörgensen, *J. pr.* [2] 6, 82).—$(PEt_4I)_3 2BiCl_3$.—$(PEt_4I)_3 2BiI_3$: brick-red crystals (J.). The acetate is resolved by heat into PEt_3O, methyl ethyl ketone, C_2H_4, CH_4, and CO_2. The benzoate is resolved by heat into PEt_3O, phenyl ethyl ketone, and benzene (Letts a. Collie).

Tri-ethyl-phosphine methylo-iodide PEt_3MeI. From PEt_3 and MeI. Gives rise to PEt_3MeOH, to $(PEt_3MeCl)_2PtCl_4$, and also to PEt_3MeCl which decomposes above 300° into ethylene and PEt_2MeHCl (Collie, *C. J.* 53, 714).

Tri-ethyl-phosphine chloro-methylo-chloride $Et_3P(CH_2Cl)Cl$. Formed by treating PEt_3 (1 mol.) with methylene chloride (1 mol.). Further treatment with PEt_3 gives $CH_2(PEt_3Cl)_2$, which is decomposed by water into PEt_3MeCl and PEt_3O (Hofmann, *Pr.* 11, 290).

Tri-ethyl-phosphine iodo-methylo-iodide $Et_3P(CH_2I)I$. Formed in like manner from PEt_3 and methylene iodide (Hofmann, *Pr.* 10, 613). Moist Ag_2O gives $Et_3P(CH_2I)OH$ whence $(Et_3P(CH_2I)Cl)_2PtCl_4$.

Tri-ethyl-phosphine allylo-iodide $PEt_3C_3H_5I$. From PEt_3 and allyl iodide (Hofmann, *Tr.* 1860, 442). Splendid needles. Successive treatment with moist Ag_2O and hydrogen sulphocyanide gives $PEt_3C_3H_5SCy$ which crystallises with difficulty.

Tri-ethyl-phosphine propylo-chloride PEt_3PrCl. Split up by heat into $Et_2PrPHCl$ and ethylene (Collie, *C. J.* 53, 714).

Tri-ethyl-phosphine isoamylo-iodide $PEt_3C_5H_{11}I$. From PEt_3 and isoamyl iodide in ethereal solution. Purified by solution in alcohol and ppn. by ether. Gives with moist Ag_2O a hydroxide which on distillation appears to give ethane and di-ethyl-amyl-phosphine oxide. With HCl and $PtCl_4$ the hydroxide gives prisms of $(PEt_3C_5H_{11}Cl)_2PtCl_4$, sl. sol. water, insol. alcohol, and ether.

Benzylo-chloride $PEt_3C_7H_7Cl$. [178°]. Needles. Formed by heating PEt_3 with benzyl chloride at 130° in presence of alcohol. Above 300° it splits up into $C_7H_7PEt_2HCl$ and C_2H_4 (Collie, *C. J.* 53, 714). The benzyl-di-ethyl-phosphine $C_7H_7PEt_2$ so obtained boils about 253° and forms a crystalline oxide $C_7H_7PEt_2O$ [330°] and sulphide $C_7H_7PEt_2S$ [95°] (300°–310°). By treatment of $PEt_3C_7H_7Cl$ with Ag_2O, a strongly alkaline solution of $PEt_3C_7H_7(OH)$ is obtained. This base gives a very deliquescent crystalline iodide and a sparingly soluble platinochloride $(PEt_3C_7H_7Cl)_2PtCl_4$. The base $PEt_3C_7H_7(OH)$ is split up by heat into toluene and PEt_3O (Collie, *P. M.* 24, 27). The hydroxide does not form a normal carbonate, but it forms an acid carbonate which is split up by heat into toluene CO_2 and PEt_3O. The sulphate on distillation gives PEt_3O, SO_2, and $PhCH_2.CH_2Ph$. The bromide gives on distillation HBr, PEt_3HBr, $PEt_2C_7H_7HBr$, acetylene, &c. The acetate gives PEt_3O, methyl benzyl ketone, PEt_3, and benzyl acetate. The oxalate gives PEt_3O, toluene, CO_2 and CO.

Tri-ethyl-phosphine bromo-ethylo-bromide $Et_3P(CH_2.CH_2Br)Br$. [235°]. Produced, together with $C_2H_4(PEt_3Br)_2$, by adding ethylene bromide to PEt_3 mixed with twice its volume of ether until the liquid no longer gives with CS_2 the red crystals of PEt_3CS_2. The two products are separated by crystallisation from alcohol in which $C_2H_4(PEt_3Br)_2$ is much the more soluble. White unctuous elongated rhombic dodecahedra; v. sol. water, m. sol. alcohol. It gives off HBr when heated.

Reactions.—1. *Silver salts* added to its cold solution throw down only half the bromine as AgBr; on continued boiling the whole of the bromine is ppd. with formation of salts of vinyl-tri-ethyl-phosphonium.—2. Moist Ag_2O forms a solution of $Et_3P(C_2H_4OH)(OH)$.—3. *Potash* has no action in the cold.—4. *Zinc* and dilute H_2SO_4 form PEt_4Br.—5. It unites with PMe_3 forming $C_2H_4(PEt_3Br)(PMe_3Br)$.—6. PEt_3 gives $C_2H_4(PEt_3Br)_2$.—7. *Ammonia* gives rise to $C_2H_4(PEt_3Br)(NH_3Br)$; *ethylamine, diethylamine*, and *trimethylamine* act in like manner.—8. *Triethylamine* when pure has no action at 100°; but in presence of moist alcohol it forms $PEt_3(C_2H_4OH)Br$ and NEt_3HBr.

Tri-ethyl-phosphine bromo-ethylo-chloride $Et_3P(CH_2.CH_2Br)Cl$. From the preceding and AgCl. Crystallises with difficulty, v. sol. water and alcohol. $Et_3P(C_2H_4Br)ClAuCl_3$: light yellow needles (from boiling water; sl. sol. cold water).—$\{Et_3P(C_2H_4Br)Cl\}_2PtCl_4$: long monoclinic orange-yellow prisms; $a:b:c = \cdot969:1:\cdot658$. May be re-crystallised from boiling water.

Tri-ethyl-phosphine bromo-ethylo-iodide $Et_3P(CH_2.CH_2Br)I$. Scales, sl. sol. cold water. Obtained by decomposing the sulphate by BaI_2. The sulphate obtained from the bromide by Ag_2SO_4 forms long white needles. The

hydroxide $Et_3P(CH_2.CH_2Br)OH$ obtained by treating the sulphate with baryta is unstable.

Tri-ethyl-phosphine chloro-ethylo-chloride $PEt_3(CH_2CH_2Cl)Cl$. From PEt_3 and ethylene chloride in the cold.—$(PEt_3(C_2H_4Cl)Cl)_2PtCl_4$: orange-yellow crystals.

Tri-ethyl-phosphine oxy-ethylo-hydroxide $PEt_3(CH_2.CH_2OH)OH$. From $PEt_3(C_2H_4Br)Br$ and moist Ag_2O. Very deliquescent syrup. When strongly heated it is resolved into ethylene, PEt_3, and water. It forms the following salts :—$PEt_3(C_2H_4OH)Cl$: indistinctly crystalline; converted by PCl_5 into $PEt_3(C_2H_4Cl)Cl$, and by PBr_5 into $PEt_3(C_2H_4Br)Cl$.—$PEt_3(C_2H_4OH)AuCl_4$: golden needles, sl. sol. boiling water.—$\{PEt_3(C_2H_4OH)Cl\}_2PtCl_4$: orange-yellow octahedra, v. sol. hot water.—$PEt_3(C_2H_4OH)I$: long needles which decompose at 100°.

Tri-ethyl-phosphine vinylo-compounds. These are formed by prolonged boiling of tri-ethyl-phosphine bromo-ethylo compounds with silver salts. Thus silver acetate gives rise to $PEt_3(CH{:}CH_2)OAc$ whence platinic chloride gives octahedra of $\{PEt_3(CH{:}CH_2)Cl\}_2PtCl_4$. The hydroxide $PEt_3(C_2H_3)OH$ is formed when $HO.PEt_3.C_2H_4.NH_3.OH$ is heated.

Hexa-ethyl-di-phosphine ethyleno-dibromide $(Et_3P)_2C_2H_4Br_2$. Prepared by treating ethylene bromide (1 vol.) with PEt_3 (3 vols.). Also from $Et_3P(C_2H_4Br)Br$ and ethylene bromide in alcoholic solution at 100°. White needles, v. sol. water and alcohol, insol. ether; permanent in the air. A boiling alcoholic solution dissolves Ag_2O and on cooling deposits crystals of $(Et_3P)_2C_2H_4Br_2AgBr$ which is resolved by water into AgBr and $(Et_3P)_2C_2H_4Br_2$.

Hexa-ethyl-di-phosphine ethyleno-dihydroxide $(Et_3POH)_2C_2H_4$. Prepared by adding excess of Ag_2O and a little water to a solution of the preceding dibromide or of the corresponding di-iodide. Highly caustic deliquescent syrup which absorbs CO_2 from the air forming a crystalline carbonate. Its solution begins to decompose at 160°; at 190° some of it forms an isomeric base, and at 250° it is completely decomposed into PEt_3, ethylene, PEt_3O, and water. Its solution reacts with metallic salts in the same way as KOH, excepting that the pp. of zinc hydrate is not soluble in excess and that stannous and antimonious salts give double-salts crystallising in interlacing needles. It expels NH_3, amines, and PEt_3 from their salts. It dissolves sulphur forming a yellow liquid which gives off H_2S when acidified. Its solution also dissolves iodine forming a colourless solution apparently containing its iodide and iodate.

Salts.—$(Et_3P)_2(C_2H_4)Cl_2$: from the hydroxide and HCl, from the dibromide and AgCl, or from PEt_3 and ethylene chloride. Deliquescent pearly flat laminæ; v. sol. water and alcohol, insol. ether. KOH ppts. it unaltered from its solutions.—$(Et_3P)_2(C_2H_4)_2Au_2Cl_8$: golden needles, sl. sol. cold water, v. sol. boiling alcohol.—$\{(Et_3P)_2C_2H_4Cl_2\}_23HgCl_2$: crystals, sl. sol. water and alcohol.—$(Et_3P)_2(C_2H_4)_2PtCl_6$: monoclinic prisms (from boiling HClAq); nearly insol. boiling water.—$(Et_3P)_2(C_2H_4)_2Cl_2(SnCl_2)_2$? large prisms.—$(Et_3P)_2(C_2H_4)I_2$: [231°]; trimetric needles. S. 458 at 100°; 3·08 at 12°. Sl. sol. alcohol, insol. ether. Potash ppts. it in the crystalline state even from very dilute solutions.—$(Et_3P)_2(C_2H_4)I_2ZnI_2$: long needles (from hot water).—$(Et_3P)_2(C_2H_4)(ClO_4)_2$: very long needles, detonates above 100°.

Ethylene-tri-ethyl-phosphammonium compounds.—$Et_3PBr.CH_2.CH_2.NH_3Br$. Formed from $Et_3P(CH_2CH_2Br)Br$ and alcoholic NH_3 at 100°. Deliquescent. — $Et_3PCl.CH_2.CH_2.NH_3Cl(AuCl_3)_2$: slender golden needles, sl. sol. water.—$Et_3PCl.CH_2.CH_2.NH_3ClPtCl_4$: pale-yellow trimetric prisms, sl. soluble in boiling water.—$Et_3P(OH).C_2H_4.NH_3OH$. From the bromide and moist Ag_2O. Separated by KOH as oily drops. Split up by heat into NH_3, water, and $Et_3P(C_2H_3).OH$.

Ethylene-tetra-ethyl phosphammonium compounds $Et_3PBr.C_2H_4.NEtH_2Br$. Formed from $Et_3PBr(C_2H_4Br)$ and ethylamine. The corresponding hydroxide is oily. The iodide $Et_3PI.C_2H_4.NEtH_2I$ forms needles, v. sol. water, slightly soluble in alcohol, insol. ether. — $Et_3PCl.C_2H_4.NEtH_2Cl(AuCl_3)_2$: golden sparingly soluble needles. — $Et_3PCl.C_2H_4.NEtH_2ClPtCl_4$: orange monoclinic tables.

Ethylene-penta-ethyl phosphammonium bromide $Et_3PBr.C_2H_4.NEt_2HBr$. From diethylamine and $Et_3PBr(C_2H_4Br)$.—May be converted into $Et_3PCl.C_2H_4.NEt_2HClPtCl_4$: rectangular plates.

Ethylene-methyl-tri-ethyl-phosphammonium bromide $Et_3PBr.C_2H_4.NMeH_2Br$. Prepared from $Et_3PBr(C_2H_4Br)$ and methylamine. Gives $Et_3PCl.C_2H_4.NMeH_2ClPtCl_4$: long needles; v. sl. sol. water.

Ethylene-tri-methyl-tri-ethyl-phosphammonium bromide $Et_3PBr.C_2H_4.NMe_3Br$. Formed in like manner, using trimethylamine. — $Et_3PCl.C_2H_4.NMe_3ClPtCl_4$: needles.

Ethylene-hexa-ethyl-phospharsonium bromide $Et_3PBr.C_2H_4.AsEt_3Br$. Prepared from $Et_3PBr(C_2H_4Br)$ and $AsEt_3$. Cold moist Ag_2O gives $Et_3P(OH).C_2H_4.AsEt_3(OH)$ which on boiling splits up into $Et_3P(OH).C_2H_4.OH$ and $AsEt_3$.—$Et_3PCl.C_2H_4.AsEt_3ClPtCl_4$: orange-red triclinic prisms (from boiling HClAq); nearly insol. water.

ETHYL - PHOSPHINIC ACID *v.* ETHANE PHOSPHONIC ACID.

ETHYL PHOSPHITES

Mono-ethyl phosphite $P(OEt)(OH)_2$. *Ethyl-phosphorous acid.* Formed by adding PCl_3 drop by drop to dilute alcohol in the cold. The product is evaporated *in vacuo* and saturated with $BaCO_3$ (Wurtz, *A. Ch.* [3] 16, 218). The free acid is very unstable, splitting up in solution into alcohol and phosphorous acid.—$BaH_2A''_2$: amorphous deliquescent mass. In solution it is resolved gradually by atmospheric oxidation into alcohol and barium metaphosphate. It is v. sol. water and alcohol, but ppd. from its alcoholic solution by ether.—BaA''. Obtained by treating Et_3PO_3 (1 mol.) with hot aqueous BaO_2H_2 (1 mol.). Amorphous. Resolved by boiling water into $BaHPO_3$ and alcohol (Railton, *C. J.* 7, 219).—$PbH_2A''_2$: unctuous scales, permanent in the air; sol. water and alcohol, insol. ether.

Di-chloride $EtO.PCl_2$. (118° cor.). S.G. $^{0}_{4}$ 1·3053 (Thorpe, *C. J.* 37, 346). Formed by treating Et_3PO_3 with PCl_3, avoiding excess of Et_3PO_3 (Chambon, *Jena. Zeit.* [2] 3; *2nd Suppl.* 97). Formed also when dry alcohol is treated with PCl_3 (Menschutkin, *A.* 139, 343).

Reactions.—1. *Water* forms HCl, alcohol, and

H_3PO_3.—2. *Bromine* gives EtBr and $POCl_2Br$.—3. Et_3PO_3 reacts forming Et_3PO_4, phosphorus, and EtCl.—4. *Heated* to 165° in a sealed tube it is resolved into EtCl, free phosphorus, PCl_3 and P_2O_5.—5. Heated with H_3PO_3 there is evolved EtCl and HCl, while free phosphorus and H_3PO_4 remain.—6. PCl_3 does not act on it.—7. PCl_5 at 100° forms $POCl_3$, PCl_3, and EtCl (Geuther, *J.* 1876, 206).—8. PBr_5 gives $POBrCl_2$, PBr_3, and EtBr.

Di-ethyl phosphite $(EtO)_2POH$. The barium salt BaA'_2 is formed by adding a hot solution of baryta (1 mol.) to Et_3PO_3. It forms a very deliquescent crystalline mass; extremely sol. water, sl. sol. alcohol. It does not decompose at 108°. Aqueous K_2SO_4 converts it into the deliquescent salt KA'. The free acid has not been isolated.

Chloride $(EtO)_2PCl$. From alcohol (2 mols.) and PCl_3 (1 mol.) (Wichelhaus, *A. Suppl.* 6, 264). May be distilled. Chlorine converts it into EtCl and $(EtO)PO{:}Cl_2$.

Tri-ethyl phosphite $(EtO)_3P$. *Phosphorous ether.* (191°). S.G. $^{12\cdot 2}$ 1·075. V.D. (in hydrogen) 5·84 (calc. 5·76). PCl_3 (1 mol.) diluted with five times its bulk of ether is added by small portions to NaOEt (3 mols.). The ether is distilled off, and the residue distilled from an oil-bath at 200°. It is rectified in a current of hydrogen (Railton, *C. J.* 7, 216). At the same time another body $P_2O_8C_{14}H_{36}$ is formed (157·5° cor.). S.G. ^{14} ·960. This is best formed from dry NaOEt (4 mol.) and PCl_3 (1 mol.), both in ether (Geuther, *A.* 224, 277). It has a pleasant smell, and when distilled it slowly splits up thus:

$$P_2O_8C_{14}H_{36} = PO_3Et_3 + PO_4Et_3 + HOEt.$$

It is not decomposed by water at 100°.

Properties. — Phosphorous ether has a pleasant odour (G.). It is sol. water, alcohol, and ether, and burns with a bluish flame.

Reactions.—1. Heated with *baryta-water* it gives $Ba(Et_2PO_3)_2$ and $BaEtPO_3$.—2. *Caustic potash* gives phosphorous acid and alcohol.—3. Gradual oxidation by *nitric* acid gives phosphoric and oxalic acids.—4. It absorbs *oxygen*, especially on warming, forming Et_3PO_4.—5. On *distillation* it gives PH_3, phosphoric acid, and probably ethylene.—6. PCl_3 gives $EtOPCl_2$; a smaller quantity of PCl_3 gives Et_3PO_4, phosphorus, and EtCl.—7. PCl_5 gives $(EtO)POCl_2$, EtCl, and PCl_3 (Chambon).—8. *Bromine* forms EtBr and $(EtO)_2POBr$.

Combination.—$Et_3PO_3PtCl_2$. [83°]. Formed from PCl_3, alcohol, and $PtCl_2$ (Schützenberger, *Bl.* [2] 18, 101). Yellow prisms. Its ethereal solution absorbs ethylene forming oily $(Et_3PO_3PtCl_2)_2C_2H_4$. CO forms in like manner $(Et_3PO_3PtCl_2)_2CO$. Ammonia passed into the ethereal solution of $Et_3PO_3PtCl_2$ ppts. colourless crystals of $Et_3PO_3PtCl_2N_2H_6$. The following compounds of ethyl phosphite have also been described $(Et_3PO_3)_2PtCl_2$: prisms.—$Et_3PO_3.PtCl_2PCl_3$.—$(Et_3PO_3)_2PtCl_2N_2H_6$. — $Et_3PO_3PtCl_2Br_2$. — $(Et_3PO_3)_2PtCl_2Br_2$. — $Et_3PO_3Pt_2Cl_4$ (Cochin, *Bl.* [2] 31, 499).—$Et_3PO_3PtCl_4$ (Pomey, *Bl.* [2] 35, 421).

TRI-ETHYL-PHOSPHOBETAÏNE *v.* Tri-ethyl-phosphine, *Reactions* 12 to 15.

ETHYL-PHOSPHOR-DICHLORIDE is Ethyl-*di-chloro*-phosphine.

ETHYL-PHOSPHORIC ACID *v.* Ethyl phosphates.

ETHYL-PHOSPHOROUS ACID *v.* Ethyl phosphites.

DI-ETHYL-PHTHALIDE
$C_6H_4<\genfrac{}{}{0pt}{}{CEt_2}{CO}>$ [52°]. Formed by adding $ZnEt_2$ to phthalyl chloride mixed with benzene (Wischin, *A.* 143, 260; Friedländer, *Z. K.* 6, 590; V. Meyer, *B.* 17, 818). Large dimetric crystals (from ether). Insol. water, v. e. sol. alcohol and ether. Does not react with $KHSO_3$ or hydroxylamine.

ETHYL-PHTHALIMIDE *v.* *Ethylimide* of Phthalic acid.

ETHYL-PHTHALIMIDYL-BENZYL is described as Benzylidene-phthalethylimidine.

a-ETHYL-HOMO-o-PHTHALONITRILE *v.* o-Cyano-phenyl-butyronitrile.

ETHYL-PICRAMIDE *v.* Tri-nitro-ethyl-aniline.

ETHYL-PIPERIDINE *v.* Ethyl-pyridine hexahydride.

ETHYL PROPARGYL OXIDE *v.* Propargyl alcohol.

ETHYL-ISO-PROPENYL-OXIDE $C_5H_{10}O$ *i.e.* $Et.O.C_3H_5$. (63°). S.G. ^{0} ·79; ^{20} ·769. Formed by heating propylene bromide and alcoholic potash in sealed tubes to 170° or by treating propinene $Me.C{\equiv}CH$ in the same way (Faworsky, *J. pr.* [2] 37, 533). Colourless mobile liquid. Yields on decomposition with dil. H_2SO_4 ethyl alcohol and acetone.

ETHYL-PROPIONYL-PROPIONIC ACID. *Methyl ether* $C_9H_{16}O_3$ *i.e.*

$$CH_3.CH_2.CO.CMeEt.CO_2Me.$$

(208°). From methyl-propionyl-propionate, EtI, and NaOEt at 100° (Pingel, *A.* 245, 84).

ETHYL-PROPIONYL-UREA *v.* *Propionyl derivative* of Ethyl-urea.

ETHYL-PROPYL ACETAL. Described under Aldehyde.

ETHYL-PROPYL-ACETIC ACID *v.* Heptoic acid.

ETHYL-PROPYL-ACETYLENE *v.* Heptinene.

DIETHYL-PROPYL-ALKINE *v.* Di-ethyl-oxypropyl-amine.

TRI-ETHYL-PROPYL-AMMONIUM IODIDE $C_9H_{22}NI$ *i.e.* NEt_3PrI. From NEt_3 and PrI (Mendius, *A.* 121, 136). Needles.—$B'_2H_2PtCl_6$: octahedra.

ETHYL-PROPYL-ANILINE $C_6H_5.NEtPr$. [216° uncor.] Liquid. Formed by the action of ethyl bromide upon propyl-aniline, or of propyl bromide upon ethyl-aniline.—B'HCl: crystals, [131° uncor.] (Claus a. Hirzel, *B.* 19, 2787).

Methylo-iodide *v.* *Propylo-iodide of* Methyl-ethyl-aniline.

ETHYL-PROPYL-BENZENE [3:1]$C_6H_4(C_3H_7)Et$. (194°). S.G. ^{12} ·8588. V.D. 5·37. Occurs in resin oil (Renard, *C. R.* 97, 328). Gives isophthalic acid on oxidation. H_2SO_4 gives a sulphonic acid of which the Ba salt $(C_{11}H_{15}SO_3)_2Ba$ aq crystallises in plates.

ETHYL-PROPYL-CARBINOL *v.* Hexyl alcohol.

Ethyl-di-propyl-carbinol *v.* Ennyl alcohol.

ETHYL-PROPYL-CARBONATE $(C_2H_5O).CO.(OC_3H_7)$. (146° cor.). S.G. $\frac{20}{4}$ ·9516. Colourless liquid. Formed by adding $AlCl_3$ to a mixture of propyl alcohol and ethyl chloroformate (Pawlewski, *B.* 17, 1606).

ETHYL-PROPYLENE *v.* Amylene.

ETHYL PROPYL ETHER *v.* ETHYL PROPYL OXIDE.

DI-ETHYL-PROPYL-GLYCOLLINE *v.* DI-ETHYL-DI-OXYPROPYL-AMINE.

ETHYL PROPYL-GLYOXALINE $C_3H_2(C_2H_5)(C_3H_7)N_2$. *Oxal-propyline.* (231°). S.G. ^{17} ·952. V.D. 4·8 (obs.).

Formation.—1. From di-propyl-oxamide by the action of PCl_5, the resulting chloro-ethyl-propyl-glyoxaline (*v.* p. 66) being reduced by HI and phosphorus (Wallach, *A.* 214, 314; *B.* 14, 423).—2. By the action of propyl bromide on secondary (para)-ethyl-glyoxaline $B'_2H_2Cl_2PtCl_4$ (Wallach, *B.* 16, 543; Radziszewski, *B.* 16, 491).

Properties.—Liquid, with narcotic smell; miscible with water. Its zinc double salt distilled with lime yields NH_3, an olefine, pyrrol, and a basic liquid (c. 253°).

Salts. — $B'_2H_2PtCl_4$: orange laminæ. — $B'_2H_2ZnCl_4$: [92°]; prisms.

Methylo-compounds B'MeI: needles, sol. water.—$B'_2Me_2PtCl_6$: plates.

Ethyl-isopropyl-glyoxaline $C_3H_2(C_2H_5)(C_3H_7)N_2$. *Oxal-ethyl-butyline.* (220°). S.G. ^{18} ·959 (Rieger, *M.* 9, 607).

DI-ETHYL PROPYLIDENE DISULPHONE $CMe_2(SO_2Et)_2$. *Sulfonal. Di-ethyl-sulphone-di-methyl-methane. Propane disulphinic ether.* [126°]. (c. 300°). S. 1 in the cold; 5 at 100°.

Preparation.—1. By action of sodium on a benzene solution of ethylidene-di-ethyl-sulphone previously mixed with methyl iodide.—2. By boiling an alcoholic solution of ethylidene-di-ethyl-sulphone with methyl iodide and alcoholic potash.—3. By treating $EtS.SO_2.OH$ with acetone and HCl, the product $CMe_2(SEt)_2$ being oxidised by $KMnO_4$ (Baumann, *B.* 19, 2808).

Properties.—Thick prisms; sl. sol. cold water and alcohol; m. sol. hot water. Used as a soporific, being said to have no concomitant effects. Does not evolve hydrogen when sodium is added to its benzene solution (E. Fromm, *B.* 21, 187).

ETHYL *n*-PROPYL KETONE $C_6H_{12}O$ *i.e.* Et.CO.Pr. Mol. w. 100. (c. 123°). S.G. $^{17\cdot5}$ ·818.

Formation.—1. Occurs among the products of the distillation of calcium butyrate (Friedel, *A.* 108, 125).—2. From butyryl chloride and $ZnEt_2$ followed by water (Butlerow, *Bl.* [2] 5, 17). 3. By distilling a mixture of calcium propionate and calcium butyrate (Völker, *B.* 8, 1019).

Properties.—Liquid. Does not unite with $NaHSO_3$ in the cold, but on heating the mixture and allowing it to cool a crystalline compound is formed, which is resolved by water into its constituents. Chromic acid mixture gives only propionic acid according to Popoff (*A.* 161, 285), but Wagner (*J. R.* 16, 660) obtained acetic and butyric acids also. Sodium amalgam reduces it to a secondary hexyl alcohol and a pinacone $C_{12}H_{26}O_2$. Zinc and MeI forms CMeEtPrOH (140°) (Sokoloff, *J. R.* 1887, 587).

Ethyl isopropyl ketone Et.CO.Pr. (118°) (P.); (114°) at 745 mm. (W.). S.G. $\frac{0}{0}$ ·830; $\frac{18}{0}$ ·814 (W.). From isobutyryl chloride and $ZnEt_2$ (Butlerow, *A.* 189, 44; Pawloff, *J. R.* 8, 242; Wagner, *J. R.* 16, 697). Liquid. Does not combine with $NaHSO_3$. Gives, on oxidation by chromic acid, propionic, acetic, and isobutyric acids (W.).

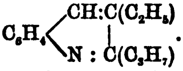
ETHYL PROPYL OXIDE $C_5H_{12}O$ *i.e.* Et.O.Pr. (63·6°). S.G. $\frac{0}{0}$ ·7545 (Dobriner, *A.* 243, 4); $\frac{20}{4}$ ·7386 (Brühl, *A.* 200, 177). S.V. 127·1. C.E. (0°–10°) ·00134 (D.). μ_β 1·3740 (B.). R_∞ 42·86 (B.). *Critical temperature* 233° (Pawlewsky, *B.* 16, 2634). Formed by distilling a mixture of ethyl alcohol and propyl alcohol with H_2SO_4; Et_2O being also formed (Norton a. Prescott, *Am.* 6, 245). Also from *n*-propyl bromide and NaOEt in alcohol, much propylene being given off.

Ethyl isopropyl oxide Et.O.Pr. (54°) (Markownikoff, *A.* 138, 374); (48°) (R.). S.G. ^{0} ·745 (M.). Formed by heating isopropyl iodide (1 vol.), triethylamine (2 vols.), and alcohol (4 vols.) at 150° (Reboul, *J.* 1881, 409). Dilute H_2SO_4 at 150° splits it up into EtOH and isopropyl alcohol (Eltekoff, *Bn.* 1, 298).

DI-ETHYL-PROPYL-PHOSPHINE PEt_2Pr. (146°–149°). From PEt_3PrCl, by distilling and treating the product with NaOHAq (Collie, *C. J.* 53, 721).

ETHYL-PROPYL-PINACONE *v.* DI-OXY-DODECANE.

(*Py.* 2:3)-**ETHYL-PROPYL-QUINOLINE**



$$C_6H_4\left\langle\begin{matrix}CH{:}C(C_2H_5)\\ \vert\\ N : C(C_3H_7)\end{matrix}\right.$$

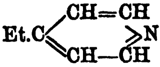
. (291° at 720 mm.). Prepared by slowly adding *n*-butyric aldehyde (100 g.) to a cooled mixture of aniline (60 g.) and fuming HCl (120 g.). Colourless liquid. Volatile with steam. V. sol. alcohol, ether, &c., nearly insol. water. On oxidation with CrO_3 it gives (*Py.* 2)-ethyl-quinoline-(*Py.* 3)-carboxylic acid.

Salts.—B'HCl 2aq: flat triclinic tables.—$B'HNO_3aq$: long white needles. — $B'H_2SO_4$: easily soluble concentric needles.—$B'_2H_2Cl_2PtCl_4$: yellow needles, sol. hot, insol. cold, water.—$B'_2H_2Cr_2O_7$: long orange-yellow needles.—$B'C_6H_2(NO_2)_3OH$: [163°]; glistening yellow plates or needles, sol. hot water and hot alcohol, very sparingly sol. cold alcohol, insol. cold water.

Methylo-iodide BMeI aq: [172°]; yellow needles; v. sol. water and alcohol, insol. ether. —$(B'MeCl)_2PtCl_4$: orange-yellow needles (Kahn, *B.* 18, 3361).

ETHYL-PROPYL-DI-THIO-CARBONATE *v.* ETHYL CARBONATES.

(γ)- or (*Py.* 1)-**ETHYL-PYRIDINE**



$$Et.C\left\langle\begin{matrix}CH{=}CH\\ \\ CH{-}CH\end{matrix}\right\rangle N$$

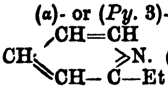
(166°). S.G. ^{0} ·9522; ^{22} ·9358.

Formation.—By heating pyridine ethylo-iodide in sealed tubes to 320° and separating the (*Py.* 3)- and (*Py.* 1)- isomerides by means of the platino-chlorides or ferrocyanides. The salts of the *Py.* 1 base are least soluble (Ladenburg, *A.* 247, 18; *cf. B.* 16, 2059).

Properties.—Unpleasant smelling liquid, sl. sol. water. Yields on oxidation with permanganate isonicotinic acid [303°].

Salts.—$(C_7H_9NHCl)_2PtCl_4$: [208°]; plates, sl. sol. water.—$B'HAuCl_4$: [138°]; golden-yellow prisms.—Picrate: [163°]; thin yellow needles.—Mercuric chloride double salt [150°]. According to O. de Coninck this base (or the mixture of isomerides) occurs in coal-tar lutidine (*C. R.* 98, 235).

(α)- or (*Py.* 3)-**Ethyl-pyridine**



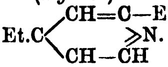
(148·5° cor.) at 752 mm. S.G. $\frac{0}{0}$ ·9498.

Preparation.—3 g. of pyridine are heated for an hour with 6 g. EtI to 320°. Some ethyl-benzene is formed. The acid contents of the tube are distilled from a copper retort with steam. The residue is then supersaturated with NaOHAq and distilled until the distillate is no longer alkaline. The base is then separated by means of solid KOH and fractionated. Purified by means of gold salt, which is decomposed by SH_2 (Ladenburg, *A.* 247, 14). (*Py.* 1)- and (*Py.* 3)-ethyl pyridines cannot be separated by fractionation.

Properties.—Colourless liquid, sl. sol. water, miscible with alcohol. It gives picolinic acid on oxidation.

Salts.—$(C_7H_9NHCl)_2PtCl_4$: [164°]; orange-yellow plates.—$C_7H_9N.HClAuCl_3$: [121°]; yellow plates, v. sol. water.—Picrate: $B'.C_6H_2(NO_2)_3OH$. [110°].

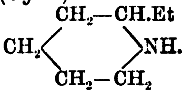
(*Py.* 1:3)-**Di-ethyl-pyridine**



(188°). S.G. $\frac{0}{0}$ ·9338. Is formed, together with (*Py.* 1)- and (*Py.* 3)- ethyl pyridine by the action of EtI on pyridine (Ladenburg, *A.* 247, 48). Colourless liquid with a very unpleasant odour, sl. sol. water. It yields lutidinic acid [235°] on oxidation.

Salts.—$(C_9H_{13}NHCl)_2PtCl_4$: [171°]; orange-yellow prisms, sl. sol. water. — Picrate: $C_9H_{13}N.C_6H_2(NO_2)_3OH$: [100°]; prisms (from water), plates (from alcohol).

(α)- or (*Py.* 3)-**ETHYL-PYRIDINE HEXAHYDRIDE**

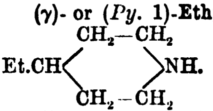


Ethyl-piperidine. (145°). S.G. ·8674. Formed by reducing (*Py.* 3)-ethyl pyridine with sodium and alcohol (Ladenburg, *A.* 247, 70; *B.* 18, 2963). Liquid smelling of pyridine hexahydride.

Reactions.—1. Forms with MeI a *ν*-methyl derivative.—2. Br and NaOHAq convert it into a base containing 2H less (*cf. B.* 20, 1645).

Salts.—$(C_7H_{15}N.HCl)_2PtCl_4$: [178°]; plates m. sol. water.

(γ)- or (*Py.* 1)-**Ethyl-pyridine hexahydride.**



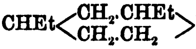
(γ)-*Ethyl-piperidine.* (158°). S.G. $\frac{0}{0}$ ·8759. Formed by reducing (*Py.* 1)-ethyl pyridine with sodium and absolute alcohol (Ladenburg, *A.* 247, 72; *cf. C. R.* 98, 516). Liquid with an unpleasant odour. More soluble in cold than in hot water. Its hydrochloride acts physiologically like coniine (Filehne, *B.* 16, 739).

Salts.—$(C_7H_{15}NHCl)_2PtCl_4$: [174°]; orange-coloured plates, m. sol. water.—$B'.HCl.AuCl_3$: [105°]; golden-yellow plates sl. sol. cold, v. sol. hot water.

Methyleno-di-iodide $C_8H_{17}NI_2$. Formed by heating ethyl-piperidine with methylene-iodide. It forms sparingly soluble yellow plates. Only one I atom can be removed by Ag_2O, or replaced by Cl by means of AgCl.

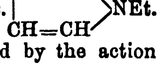
The *chloro-iodide* $C_8H_{17}NICl$ is formed from the di-iodide by AgCl.—$(C_8H_{17}NICl)_2PtCl_4$: orange crystals.—$(C_8H_{17}NICl)AuCl_3$: small yellow crystals (Ladenburg, *B.* 14, 1343).

(*Py.* 1,3)-**Di-ethyl-pyridine hexahydride**



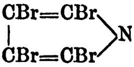
$CHEt<^{CH_2.CHEt}_{CH_2.CH_2}>NH$. (c. 176°). S.G. $\frac{0}{0}$ ·8722. Formed by reducing (*Py.* 1,3)-di-ethyl-pyridine with sodium and alcohol (Ladenburg, *A.* 247, 97).—$B'_2H_2PtCl_6$. [174°].

ETHYL-PYRROLE C_6H_9N *i.e.*



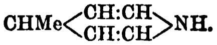
(131°). S.G. $\frac{12}{}$ ·888. Prepared by the action of ethyl iodide on pyrrole potassium. Formed also by distilling neutral ethyl-ammonium mucate or saccharate (C. A. Bell, *B.* 9, 935; Bell a. Lapper, *B.* 10, 1962; *cf.* Lubavin, *Z.* [2] 5, 399). Formed also by distilling ethyl-succinimide with zinc-dust (Bell, *B.* 13, 878). Colourless liquid; insol. water, miscible with alcohol and ether. Its vapour turns acidified pine-wood red. By long boiling with HCl it gives a red powder of the constitution $C_{16}H_{24}N_2O_2$ [165°–170°]. Potassium does not attack it. Its alcoholic solution gives a pp. with $HgCl_2$.

Tetra-bromo- derivative



[90°]. Colourless needles. Insol. water, sol. alcohol. Prepared by the action of Br on ethyl-pyrrole (Bell, *B.* 11, 1810).

Ethyl-pyrrole C_4H_4EtN? (164°). Formed by adding $ZnCl_2$ (12 g.) to a mixture of pyrrole (50 g.) and paraldehyde (50 g.), the reaction beginning at once with evolution of heat (Dennstedt a. Zimmermann, *B.* 19, 2189). Colourless, but turns brown in air. Conc. HCl at 130° appears to give



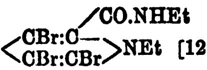
$CHMe<^{CH:CH}_{CH:CH}>NH$.

Acetyl derivative $C_4H_3Et.NAc$. (225°). Formed by boiling ethyl-pyrrole with Ac_2O and NaOAc. An isomeric acetyl derivative [47°] (250°) is formed at the same time. Benzoic aldehyde and potash converts the acetyl derivative into $C_4H_3Et.N.CO.CH:CHPh$ [150°].—$C_4H_2AgEtNAc$.

ETHYL-PYRROLE-AZO- *v.* Azo- COMPOUNDS.

ETHYL-PYRROLE CARBOXYLIC ACID $C_4H_3EtN.CO_2H$. [78°]. Formed by heating its ethylamide with alcoholic potash at 120° (Bell, *B.* 10, 1864). Slender silky needles (from hot water). Volatile with steam. Above 100° it splits up into CO_2 and ethyl-pyrrole. Boiling dilute HCl decomposes it in like manner. Fe_2Cl_6 gives a red colour.—AgA': needles (from hot water).

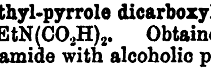
Ethylamide $C_9H_{14}N_2O$ *i.e.* $C_4H_3EtN.CONHEt$. *Di-ethyl-carbopyrrolamide.* [44°]. (270°). Formed, together with ethyl-pyrrole and the diethylamide of ethyl-pyrrole di-carboxylic acid by heating ethylamine mucate in a paraffin-bath (Bell). Prisms (from water). Soluble in conc. HClAq without change; even boiling aqueous alkalis have little action, but it is saponified by alcoholic KOH at 125°. Bromine water gives a pp. of the tri-bromo- derivative

$C_9H_{11}Br_3N_2O$ *i.e.* 
$\left\langle\begin{array}{l}CBr{:}C\diagup CO.NHEt\\ CBr{:}CBr\end{array}\right\rangle NEt$ [121°] while $C_9H_{12}Br_2N_2O_3$ [197°] remains dissolved (Bell, *B.* 11, 1813).

Ethyl-pyrrole dicarboxylic acid $C_4H_2EtN(CO_2H)_2$. Obtained by heating its ethylamide with alcoholic potash at 130° (Bell). Needles (from dilute alcohol). Sublimes without melting at 250°, being partly split up into ethyl-pyrrole and CO_2. Slowly split up in like manner by strong acids in the cold.—Ag_2A'': insol. water.

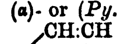
Di-ethyl-di-amide $C_4H_2EtN(CONHEt)_2$. *Tri-ethyl-dicarbopyrrolamide.* [230°]. Formed in small quantity by distilling ethylamine mucate (Bell). Needles. Insol. water, sol. conc. HClAq. May be sublimed. Saponified by alcoholic, but not by aqueous, potash.

ETHYL-QUINALDINIC ACID *v.* ETHYL-QUINOLINE-(*Py.* 3)-CARBOXYLIC ACID.

(γ)- or (*Py.* 2)-**ETHYL-QUINOLINE** $C_{11}H_{11}N$ *i.e.* 
$C_6H_4\left\langle\begin{array}{l}CH{:}CEt\\ \quad\;|\\ N{:}CH\end{array}\right.$. (273° cor.) (Reher, *B.* 20, 2734). Colourless refractive liquid. Formed by distillation of its (*Py.* 3)-carboxylic acid, CO_2 being evolved (Kahn, *B.* 18, 3370). Obtained also by reducing (*Py.* 3, 2)-chloro-ethyl-quinoline with HI in acetic acid (Baeyer a. Jackson, *B.* 13, 121); and, together with the following isomeride, by heating quinoline ethylo-iodide at 280° (Reher, *B.* 19, 2995). Gives cinchonic acid on oxidation. On reduction it yields a base boiling at (271°-275°).

Salts.—The hydrochloride is v. sol. water and deliquescent.—$B'HNO_3$: [116°]; white needles.—$B'HHgCl_3$: [154°]; white needles, v. sol. dilute HClAq.—$B'HAuCl_4$: slender yellow needles. — Chromate: red needles. — $B'_2H_2Cl_2PtCl_4$: [203°]; orange-yellow needles.—Picrate: [163°] (K.); [178°-186°] (R.); fine yellow needles.—Zinc double chloride: [195°]; concentric needles (R.).

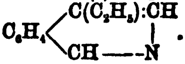
Methylo-iodide B'MeI. [149°].

(α)- or (*Py.* 3)-**Ethyl-quinoline** C_9H_6NEt *i.e.* 
$C_6H_4\left\langle\begin{array}{l}CH{:}CH\\ \quad\;|\\ N.CEt\end{array}\right.$. (258° cor.). Formed by distilling (*Py.* 3)-ethyl quinoline (*Py.* 1)-carboxylic acid with 5 times its weight of soda-lime (Döbner, *A.* 242, 272; Reher, *B.* 19, 2995; 20, 2734). Formed also by heating quinoline ethyl-iodide (*v. supra*).

Properties.—Colourless hygroscopic oil. Sl. sol. water, v. sol. alcohol and ether. Gives quinoline (*Py.* 3)-carboxylic (quinaldinic) acid on oxidation. May be reduced by tin and HCl to a tetrahydride (c. 261°), which forms a crystalline hydrochloride.

Salts.—The chloride, nitrate, and sulphate are v. sol. water. The chloride and nitrate are efflorescent. The chromate crystallises in red needles.—$(B'HCl)_2PtCl_4$ 2aq: [189°]; orange-red needles or tables, sl. sol. water.—$B'HHgCl_3$: [118°]; slender needles.—$B'HAuCl_4$: [142°]; canary-yellow needles.—$B'_2H_2SnCl_4$ 2aq: crystalline. — Picrate $B'.C_6H_3N_3O_7$: [148°]; lemon-yellow needles (from alcohol) sl. sol. water.

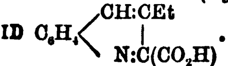
Methylo-iodide B'MeI: [180°]; greenish-yellow needles (from alcohol).

Ethyl(?)-isoquinoline $C_{11}H_{11}N$ probably 
$C_6H_4\left\langle\begin{array}{l}C(C_2H_5){:}CH\\ \qquad\qquad\;\,|\\ CH\text{——}N\end{array}\right.$. [65°]. (275° at 264 mm.). Crystalline solid. Formed by complete dechlorination of di-chloro-ethyl(?)-isoquinoline by heating with HI and P at 200°.

Salts.—$B'_2H_2Cl_2PtCl_4$ 2aq: orange-yellow flat needles.—$B'_2H_2Cr_2O_7$: orange-red glistening needles (Gabriel, *B.* 20, 1207).

Di-ethyl-quinoline $C_9H_5Et_2N$. (284° cor.). Obtained as a by-product in the ethylation of quinoline by heating its ethylo-iodide at 285° (Reher, *B.* 19, 2995). Liquid, smelling like quinoline. On oxidation with chromic mixture it gives an acid [190°].—$B'_2H_2PtCl_6$: [217°]; orange-red needles, blackens before melting.—$B'HHgCl_3$: [116°]; needles.

References.—BROMO-, CHLORO, and OXY-ETHYL-QUINOLINE.

(*Py.* 2)-**ETHYL-QUINOLINE**-(*Py.* 3)-**CARBOXYLIC ACID** 
$C_6H_4\left\langle\begin{array}{l}CH{:}CEt\\ \quad\;|\\ N{:}C(CO_2H)\end{array}\right.$. (*Py.* 2)-*Ethyl-quinaldinic acid.* [148°]. Glistening needles (containing ½aq). Sol. alcohol and hot water, sl. sol. ether. Formed by oxidation of (*Py.* 2:3)-ethyl-propyl-quinoline with CrO_3 and H_2SO_4. On distillation it evolves CO_2 and gives (*Py.* 2)-ethyl-quinoline.

Salts.—$(A'H,HCl)_2PtCl_4$: fine needles.—Picrate: [153°]; fine yellow needles, sl. sol. water and cold alcohol.—A'Ag: amorphous white pp., or very fine microscopic needles.—A'_2Cu: bluish-green microcrystalline pp. (Kahn, *B.* 18, 3368).

(*Py.* 3:1)-**Ethyl-quinoline carboxylic acid** $C_9H_5NEtCO_2H$. (*Py.* 3)-*Ethyl-cinchonic acid.* [173°].

Preparation.—Pyruvic acid (70 g.) and propionic aldehyde (50 g.) are dissolved in alcohol, and anilin (80 g.) is gradually added, and the mixture heated on the water-bath with an inverted condenser (Döbner, *A.* 242, 270).

Properties.—Needles or plates. V. sol. alcohol, ether and hot water. Yields on heating with soda-lime (*Py.* 3)-ethyl-quinoline.

Salts.—Chloride, nitrate, and sulphate are v. sol. water.—$(B'HCl)_2PtCl_4$aq: orange-yellow needles, v. sol. water, sl. sol. alcohol, insol. ether.—AgA': pp. v. sl. sol. water.

ETHYL-QUINOLINE TETRAHYDRIDE
$C_6H_4\left\langle\begin{array}{l}CH_2{:}CH_2\\ \quad\;|\\ NEt{:}CH_2\end{array}\right.$ *v.* QUINOLINE. An isomeride is obtained by reducing (*Py.* 3)-ethyl-quinoline (*q. v.*).

(*Py.* 1)-**ETHYL-QUINOLINE SULPHONIC ACID** $C_9H_5EtN.SO_3H$. [above 315°]. Obtained by heating (γ)- or (*Py.* 1)- ethyl-quinoline with fuming H_2SO_4 (10 pts.) at 260° (Reher, *B.* 19, 2995). Slender needles, insol. alcohol, v. sol. hot water.

TRI-ETHYL-ROSANILINE *v.* TRI-ETHYL-TRI-AMIDO-DI-PHENYL-TOLYL-CARBINOL.

MONO-ETHYL SELENATE $EtHSeO_4$ *i.e.* $SO_2(OH)(OEt)$. An unstable acid obtained by treating selenic acid with alcohol (Fabian, *A.*

Suppl. 1, 244).—SrA'_2: tables.—CuA'_2 4aq: plates.

ETHYL SELENHYDRATE EtSeH. (above 100°). A liquid formed according to Wöhler and Siemens (*A.* 61, 360) when KSeH is distilled with alcohol. It has a very disgusting odour, and its alcoholic solution gives a yellow pp. with $HgCl_2$.

ETHYL SELENIDE $C_4H_{10}Se$ *i.e.* Et_2Se. (108°). Prepared by digesting equivalent quantities of P_2Se_5 and $KEtSO_4$ with a small quantity of water at 50°, the product being fractionally distilled (Von Pieverling, *A.* 185, 331). Colourless mobile liquid, smelling like a hydrocarbon. Insol. water, miscible with alcohol and ether. Its solution in dilute HNO_3 gives with HCl oily Et_2SeCl_2 whence aqueous ammonia forms crystalline $(Et_2Se)_2OCl_2$ (Joy, *A.* 86, 35).

Ethylo-iodide $SeEt_3I$. *Tri-ethyl-selonium iodide.* Slowly formed by combination of $SeEt_2$ with EtI in the cold (P.). White crystals, stable in the air, v. e. sol. water and alcohol, sl. sol. ether. Sublimes between 80° and 120°, being split up into $SeEt_2$ and EtI, which slowly recombine in the cold.

Ethylo-hydroxide $SeEt_3OH$. Formed by treating the ethylo-iodide with moist Ag_2O. Powerful base, forming a syrupy solution which absorbs CO_2 with avidity. Its salts smell like leeks and, with exception of the tartrate, are very deliquescent.

Acid tartrate $SeEt_3C_4H_5O_6$ 2aq: pale rose-red needles, v. e. sol. water, forming an acid solution.—Platinochloride $(SeEt_3Cl)_2PtCl_4$: red rhombohedra. Monoclinic according to Schimper (*Z. K.* 1, 218).—Zinc double chloride $(SeEt_3Cl)_2ZnCl_2$: from $SeCl_4$ and $ZnEt_2$ (Rathke, *A.* 152, 210).

Di-ethyl di-selenide Et_2Se_2. (186°). From $KEtSO_4$ and K_2Se_2 (Rathke). Reddish-yellow liquid with highly disgusting smell. Its solution in dilute HNO_3 gives with HCl crystals of $EtSeO_2H_2Cl$ (?); these are v. sol. water, and are reduced by SO_2 to Et_2Se_2.

ETHYL DI-SELENO-PHOSPHATE $C_6H_{15}PO_2Se$ *i.e.* $Et_3PO_2Se_2$. An oil obtained by treating P_2Se_5 with alcohol (Carius, *A.* 124, 57). Slowly decomposed by water.

ETHYL SILICATE Et_2SiO_3. (350°). S.G. ^{24} 1·079. Formed, according to Ebelmen (*A.* 57, 331), together with $Et_2Si_2O_5$, by treating $SiCl_4$ with wet alcohol. Slowly saponified by water. Friedel and Crafts (*A. Ch.* [4] 9, 5) could not obtain this ether, but found instead $Et_6Si_2O_7$ (125°–130° *in vacuo*). V.D. 12·03 (calc. 11·86). S.G. ^{0} 1·0196; ^{12} 1·0119. The ether $Et_6Si_2O_7$ is also formed by treating $SiOCl_6$ with alcohol (Friedel a. Ladenburg, *A.* 147, 362); it is converted by gaseous NH_3 into $Et_5Si_2O_6(NH_2)$ (280° *in vacuo*) and $Et_4Si_2O_5(NH_2)_2$ (Troost a. Hautefeuille, *A. Ch.* [5] 7, 472).

Ethyl ortho-silicate $C_8H_{20}SiO_4$ *i.e.* Et_4SiO_4. *Silicic ether.* (166°). S.G. ^{22} ·933 (E.); ·968 (Friedel a. Crafts, *A. Ch.* [4] 9, 5). V.D. 7·32 (calc. 7·21). Formed by pouring absolute alcohol upon $SiCl_4$ and distilling the product (Ebelmen, *A.* 57, 331). Also from alcohol and SiF_4 (Knop a. Wolf, *C. C.* 1861, 899). Colourless liquid, with ethereal odour. Burns with dazzling flame. Insol. water, but slowly decomposed by it with separation of silica. Ammonia and aqueous alkalis dissolve it. Ac_2O at 180° gives $(EtO)_3SiOAc$ (c. 190°).

Chloride $ClSi(OEt)_3$. (157°). ^{0} 1·0483. V.D. 7·05 (calc. 6·81). Formed by heating $SiCl_4$ (1 mol.) with Et_4SiO_4 (3 mols.) at 150°; by heating Et_4SiO_4 (1 mol.) with AcCl (1 mol.) at 175°; or by distilling Et_4SiO_4 with PCl_5. Limpid liquid; does not fume in the air, but is quickly decomposed by moist air or water yielding HCl and silica.

Dichloride $Cl_2Si(OEt)_2$. (137°). S.G. ^{0} 1·144. V.D. 6·76 (calc. 6·55). From Et_4SiO_4 (1 mol.) and $SiCl_4$ (1 mol.). Formed also by heating $ClSi(OEt)_3$ (1 mol.) with $SiCl_4$ (2 mols.) and distilling. Liquid resembling the preceding.

Trichloride $Cl_3Si(OEt)$. (104°). S.G. ^{0} 1·291. V.D. 6·38 (calc. 6·22). Formed by heating Et_4SiO_4 or either of the preceding chlorides with excess of $SiCl_4$ for a long time. Liquid.

Octo-ethyl tetra-silicate $Et_8Si_4O_{12}$. (270°–290°). S.G. ^{0} 1·071. V.D. 19·54. From $Si_4O_4Cl_8$ and absolute alcohol (T. a. H.). Liquid. NH_3 converts it into $Et_6Si_4O_{10}(NH_2)_2$.

ETHYL-STIBINE *v.* *Organic compounds* of ANTIMONY.

ETHYL-STILBENE *v.* ETHYL-DI-PHENYL-ETHYLENE.

Di-ethyl-stilbene *v.* DI-ETHYL-DI-PHENYL-ETHYLENE.

ETHYL-SUCCINIC ACID $CO_2H.CH_2.CHEt.CO_2H$. *Butane di-carboxylic acid.* [98°]. (243°).

Formation.—1. By boiling α-acetyl-α-ethyl-succinic ether with conc. alcoholic KOH (Huggenberg, *A.* 192, 148).—2. By oxidation of β-acetyl-propionic acid (Thorne).—3. By distilling butane tri-carboxylic acid (derived from malonic and α-bromo-butyric ethers) (Polko, *A.* 242, 121).

Preparation.— α-Acetyl-β-ethyl-succinic ether is heated with very strong potash (2:1) at 100°. Excess of the ether removed by shaking with ether, the acids are then liberated by H_2SO_4 and extracted with ether (L. T. Thorne, *C. J.* 39, 338).

Properties.—Prisms (from chloroform and petroleum ether); v. e. sol. water, alcohol, ether, and chloroform, insol. petroleum-ether.

Salts.—KHA'': v. e. sol. water, insol. alcohol.—K_2A'' ½aq: very hygroscopic.—CaA'' 2aq: prisms, v. sl. sol. water.—$CaH_2A''_2$ 3aq: sl. sol. water, insol. alcohol.—BaA'' 1½aq: v. sol. water, insol. alcohol.—SrA''.—CuA'': blue insoluble pp. —ZnA'' 2aq: v. e. sol. water, insol. alcohol.—Ag_2A'': powder; decomposes at 110°.

Methyl ether Me_2A''. (204°). S.G. $\frac{34}{34}$ 1·051. Does not solidify at −19°.

Ethyl ether Et_2A''. (225°). S.G. $\frac{21}{21}$ 1·030.

Anhydride $C_6H_8O_3$. S.G. $\frac{34}{34}$ 1·165.

Amide: [214°]; insol. cold water.

Di-ethyl-succinic acid $CO_2H.CEtH.CEtH.CO_2H$. [190°]. S. ·61 at 23°; 6·7 at 95°. Formed, together with an isomeride [140°], from xeronic acid $CO_2H.CEt{:}CEt.CO_2H$ and HI (Otto, *A.* 239, 280). Monoclinic plates, sl. sol. water, v. sol. alcohol and ether. Converted by heating with HClAq into the isomeride [129°]. —Na_2A''.—CaA'' 2aq.—CuA'' aq.—ZnA'' 2aq.

Ethyl ether Et_2A''. (234°). S.G. ^{15} ·991. Formed, together with the isomeric ether, by heating α-bromo- (or iodo-) butyric ether with finely-divided silver at 120° to 130° (Hell, *B.* 6, 28; 13, 475, 479; 22, 67; Hjelt, *B.* 20, 3078). It is well to add some MeI.

Anhydride (c. 240°).

Di-ethyl-succinic acid $CO_2H.CEtH.CEtH.CO_2H$. [129°]. S. 2·4 at 23°. This acid is obtained, together with the preceding, by heating hexane tri-carboxylic acid obtained from α-bromo-butyric and ethyl-malonic ethers by treatment with NaOEt (Hjelt; Hjelt a. Bischoff, *B.* 21, 2098; Zelinsky a. Bitschichni, *B.* 21, 3398). It is also formed by dissolving the anhydride of the preceding in water. Trimetric plates, v. sol. alcohol and ether. By heating quickly it is converted into the anhydride (246°). By heating for 8 hours at 220° it is converted into the isomeric acid [190°]. On heating with resorcin and H_2SO_4 it gives a fluoresceïn.—Na_2A''.—CaA'' aq.—CuA''aq.—ZnA'' 6aq.

ETHYL SUCCINIMIDE *v. Ethylimide of* SUCCINIC ACID.

ETHYL-SUCCINURIC ACID $C_7H_{12}N_2O_4$ *i.e.* $NHEtCO.NH.CO.C_2H_4.CO_2H$. [167°]. Formed by the action in the cold of dilute H_2SO_4 on succinyl-ethyl-urea (the compound of succinimide with cyanic ether) (Menschutkin, *B.* 7, 128). Long needles (from alcohol). Decomposed at 190° into succinimide, water, and cyanic ether. Sl. sol. water and cold alcohol.—AgA': plates or needles (from hot water).

Amide $NHEt.CO.NH.CO.CH_2.CH_2.CONH_2$. [196°]. From succinyl-ethyl-urea and alcoholic NH_3 at 100°. Needles (from alcohol). Decomposed by heating with aqueous ammonia.

DI-ETHYL-SUCCINYL-SUCCINIC ACID *v. Di-ethyl derivative of the dihydride of* DI-OXY-TEREPHTHALIC ACID.

ETHYL-SULPHAMIC ACID $HO.SO_2.NHEt$. Prepared by the action of SO_3 on ethyl-amine (Beilstein a. Wiegand, *B.* 16, 1265). Needles. Sol. water, alcohol, and ether. Not decomposed by boiling with water.

Salts.—A'_2Ca 2aq: large prisms, sol. water, alcohol, and ether.—A'_2Ba 1½aq: silvery scales. S. (90 p.c. alcohol at 18°) = 1·33, v. sol. water.—A'_2Pb: needles, sol. water and alcohol.

Di-ethyl-sulphamic acid $HO.SO_2.NEt_2$. Formed by the action of SO_3 on di-ethyl-amine. A'_2Ba 2aq: sol. water and alcohol, insol. ether (Beilstein a. Wiegand, *B.* 16, 1266).

Chloride $NEt_2.SO_2Cl$. (208°). Formed by the action of sulphuryl chloride on di-ethyl-amine hydrochloride (Behrend, *B.* 15, 1612; *A.* 222, 134). Yellow oil, v. sol. alcohol, ether, benzene, and $CHCl_3$. Heavier than water.

TETRA-ETHYL-SULPHAMIDE $SO_2(NEt_2)_2$. (250°). Formed by the action of di-ethyl-amine on di-ethyl-sulphamic chloride at 60° (Behrend, *B.* 15, 1612; *A.* 222, 135). Heavy yellow oil, v. sol. alcohol, ether, benzene, and $CHCl_3$.

ETHYL SULPHATES.

Mono-ethyl sulphate $C_2H_6SO_4$ *i.e.* $SO_2(OH)(OEt)$. S.G. $^{\underline{16}}$ 1·316.

Formation.—1. From alcohol and H_2SO_4 (Dabit, *Ann. Chem.* 34, 300; 43, 101; Sertürner, *Gilb. Ann.* 60, 53; 64, 6, 7; A. Vogel, *Gilb. Ann.* 63, 81; Gay-Lussac, *A. Ch.* [2] 13, 76; Dumas a. Boullay, *A. Ch.* [2] 36, 300; Serullas, *A. Ch.* [2] 39, 153; Liebig a. Wöhler, *A.* 1, 37; Liebig, *A.* 13, 27; Magnus, *A.* 6, 152; Marchand, *P.* 28, 454; 32, 345; 41, 595; Müller, *A. Ch.* [3] 19, 22).—2. From ethylene and H_2SO_4 (Hennell, *Tr.* 1826, 240; 1828, 365; Berthelot, *A. Ch.* [3] 43, 385; *C. R.* 36, 1098).—3. By heating ether with H_2SO_4 (Hennell a. Magnus, *P.* 27, 386).—4. From S_2Cl_2 and alcohol (Heusser, *A.* 151, 249).

Preparation.—A mixture of equal parts of strong sulphuric acid and strong alcohol is heated to about 100°, and, after standing in a warm place for 24 hours, diluted with water, and saturated with carbonate of barium or carbonate of lead; the solution is then filtered from the precipitated sulphate of barium or lead, and the filtrate carefully evaporated to the crystallising point. The crystals of baric or plumbic ethylsulphate are then redissolved in water, the solution is decomposed with an exactly equivalent quantity of sulphuric acid—or better, in the case of the lead-salt, with H_2S—and the filtrate is concentrated in a vacuum over oil of vitriol or chloride of calcium. Claesson (*J. pr.* [2] 19, 246) recommends taking 3 pts. of alcohol to 2 pts. of H_2SO_4; the yield is then 77 p.c. If the mixture be kept at 100° for more than an hour a notable amount of ether is formed, and the yield of acid is diminished (Villiers, *C. R.* 91, 124).

Properties.—Colourless syrup, miscible with water and alcohol, insol. ether. When heated it gives off ether, leaving H_2SO_4. At a higher temperature it gives off ethylene and SO_2.

Reactions.—1. The aqueous solution decomposes slowly in the cold, quickly on boiling, the products being alcohol and H_2SO_4.—2. *Alcohol* at 130°–140° yields ether and H_2SO_4.—3. MnO_2 or K_2CrO_4 give aldehyde (Jacquemin a. Liès Bodard, *J.* 1857, 345).—4. On electrolysis it yields formic and acetic acids besides H and O (Renard, *A. Ch.* [5] 17, 301).—5. The K and Ba salts are decomposed by dry HCl at about 80° completely into EtCl and the corresponding sulphate (Köhler, *B.* 11, 1929).—6. Reacts with salts of organic acids forming the corresponding ethyl ethers.

Salts.—All the salts are v. sol. water. Their aqueous solution is decomposed by boiling, but this is prevented by the addition of a few drops of aqueous KOH. When heated with conc. H_2SO_4 they give off ether, boiling dilute H_2SO_4 liberates alcohol. When heated with KOH they give off alcohol. When distilled with other salts they form ethyl ethers of those salts.—NH_4A': [62°]; very deliquescent crystals, v. sol. water, alcohol, and ether.—KA'. S. 125 at 17°. Large monoclinic tables or laminæ; *a*:*b*:*c* = ·573:·615:1; β = 80° 27' (Schabus, *J.* 1854, 560). Deliquescent, insol. alcohol and ether.—NaA' aq. [86°]. S. 164 at 17°. Very deliquescent hexagonal plates; efflorescent in warm air.—LiA' aq: deliquescent crystals.—BaA'_2 2aq: S. 109 at 17°; S.G. $^{\underline{217}}$ 2·080; monoclinic prisms; *a*:*b*:*c* = ·823:·979:1; β = 84° 39' (Schabus). The aqueous solution becomes turbid on boiling, $BaSO_4$ being ppd.—CaA'_2 2aq: S. 100 at 8°; 125 at 17°; 157 at 30°. Monoclinic scales; permanent in the air. Sl. sol. alcohol, insol. ether.—SrA'_2: v. sol. water.—CdA'_2 2aq: long prisms, v. sol. water and alcohol, insol. ether.—CoA'_2 2aq: dark-red crystals, permanent in the air, v. sol. water and alcohol, insol. ether.—CuA'_2 4aq: rectangular prisms, v. sol. water and alcohol, insol. ether.—PbA'_2 2aq: tables, v. sol. water and alcohol, having an acid reaction.—PbA$'_2$PbO. S. 185 at 17°. Amorphous, sol. water and alcohol.—MgA$'_2$4aq: crystals, v. sol. water, insol. alcohol and ether.—MnA$'_2$4aq: roseate tables, v. sol. water and alcohol, insol. ether.—NiA$'_2$2aq: very soluble green crystals.—ZnA$'_2$2aq: large tables, v. sol. water and alcohol, insol. ether.—SmA$'_3$9aq. S.G. 1·880. Large crystals, sol. water (Clève, *Bl.* [2] 43, 171).—DiA$'_3$9aq. S.G. 1·863 (C.).—AgA$'$aq: scales, sol. water and alcohol.

Chloride $EtSO_3Cl$. *Sulphuric ethoxy-chloride.* (153° cor.).

Formation.—1. From alcohol and $ClSO_3H$, along with ethyl-sulphuric acid.—2. By dropping SO_2Cl_2 into alcohol.—3. From EtCl and SO_3 (R. Williamson, *C. J.* 2, 529; 5, 576; Kuhlmann, *A.* 33, 108).—4. From $KEtSO_4$ and PCl_5.—5. From $ClCO_2Et$ and fuming H_2SO_4 (Wilm, *B.* 6, 505).

Preparation. — Ethylene is passed into $ClSO_3H$, and the product distilled *in vacuo.* The yield is 50 p.c. (M. Müller, *B.* 6, 227).

Properties.—Slightly decomposed by distilling. Insol. water. When heated with water in sealed tubes it gives Et_2O, EtCl, HCl, and H_2SO_4 (Purgold, *Z.* [2] 4, 669).

Reactions.—1. With *alcohol* it reacts chiefly thus: $EtO.SO_2Cl + EtOH = EtO.SO_2OH + EtCl$, but also according to the two equations

(*a*) $EtO.SO_2Cl + HOEt = (EtO)_2SO_2 + HCl$,
(*b*) $(EtO)_2SO_2 + HOEt = (EtO)(HO)SO_2 + Et_2O$,

the last equation taking place when there is an excess of alcohol.—2. With *methyl alcohol* the reaction is

$EtO.SO_2Cl + HOMe = MeCl + EtO.SO_2.OH$.

3. With *amyl alcohol* $EtO.SO_2Cl + C_5H_{11}OH = C_5H_{11}SO_2OH + EtCl$. It thus appears that the chloride of the smaller alcohol radicle is formed (Claesson, *J. pr.* [2] 19, 248).

Di-ethyl sulphate $C_4H_{10}SO_4$ *i.e.* $SO_2(OEt)_2$. Mol. w. 154. [c. −24°]. (118°) at 40 mm. S.G. ^{15} 1·1837. Occurs in 'heavy oil of wine,' an oily mixture sometimes obtained in the preparation of ether (Marchand, *J. pr.* 15, 1; Serullas, *A. Ch.* [2] 39, 152).

Formation.—1. By passing vapour of SO_3 into a flask containing ether surrounded by a freezing mixture. The product is washed with lime-water and rectified (Wetherill, *A.* 66, 117).—2. From dry alcohol and SO_3.—3. From Ag_2SO_4 and EtI (Stempnewsky, *J. R.* 1882, 95).—4. From $ClSO_3Et$ and alcohol (Claesson, *J. pr.* [2] 19, 257).

Preparation.—Absolute alcohol (200 g.) mixed with conc. H_2SO_4 (450 g.) is distilled very slowly until the mixture begins to froth. The distillate separates into two layers, the lower being pure Et_2SO_4 (28 g.) (Villiers, *C. R.* 90, 1291).

Properties. — Oil, smelling of peppermint. Solidifies at about −25°. It forms double compounds with sulpho-acetates, sulpho-benzoates, and isethionates, but not with acetates, benzoates, or methane sulphonates (Geuther, *A.* 218, 288).

Reactions.—1. Warm *baryta-water* converts it into $Ba(SO_4Et)_2$.—2. When heated with water it gives alcohol, H_2SO_4, and $EtHSO_4$.—3. When heated with *alcohol* it forms ether and $EtHSO_4$.—4. SO_3 gives ethionic ether and methionic ether (R. Hübner, *A.* 223, 208).—5. KHS gives mercaptan and K_2SO_4.—6. NH_3 gives NEt_4SO_4Et and $NEtH_3SO_4Et$.

Reference.—DI-BROMO-DI-ETHYL SULPHATE.

ETHYL SULPHIDE $C_4H_{10}S$ *i.e.* Et_2S. Mol. w. 90. (93° cor.). S.G. $\frac{20}{4}$ ·8368. V.D. 3·00 (calc. 3·12). H.F.p. 28,550 (*Th.*). H.F.v. 26,230 (*Th.*). R_∞ 27·64 (Nasini, *G.* 13, 301).

Formation.—1. By the action of K_2S on $KEtSO_4$, on EtCl, or on other ethyl ethers (Döbereiner, *Schw. J.* 61, 377; Regnault, *A. Ch.* [2] 71, 387; Loir, *C. R.* 26, 195; Riche, *A. Ch.* [3] 43, 297).—2. By passing the vapour of SO_2Cl_2 in a current of CO_2 over zinc ethide, and distilling the product with water (F. Gauhe, *A.* 143, 266).—3. By distilling mercury mercaptide: $Hg(SEt)_2 = HgS + Et_2S$.

Preparation.—An alcoholic solution of potash is divided into two equal parts: one part is saturated with H_2S, and then mixed with the other; the liquid is introduced into a tubulated retort; vapour of hydrochloric ether is passed through it to saturation; and heat is then gradually applied, the stream of hydrochloric ether vapour being still kept up. From the distillate, which contains alcohol and ether as well as sulphide of ethyl, the sulphide of ethyl is precipitated by water; it is then purified by washing with water, dehydrated by chloride of calcium, and rectified (Regnault).

Properties.—Oil, with alliaceous odour. Sol. alcohol. Burns readily with blue flame. Takes fire when poured into chlorine. HgO has no action on it, but lead acetate gives a yellow pp.

Reactions.—1. *Nitric acid* (S.G. 1·2) forms di-ethyl sulphoxide Et_2SO. Fuming HNO_3 forms di-ethyl sulphone (Oefele, *A.* 127, 370).—2. Boiling aqueous KOH has no action, but on distilling over solid KOH there is formed KHS and alcohol.—3. Heated with sulphur at 180° it is partly converted into Et_2S_2, Et_2S_3, Et_2S_4, and Et_2S_5 (Böttger, *A.* 223, 351).—4. S_2Cl_2 acts energetically, forming HCl, carbon, and sulphur (B.).—5. $SOCl_2$ forms similarly HCl, carbon, S, and SO_2.—6. $Cl.SO_3H$ forms HCl, carbon, S, H_2SO_4, and H_2O.—7. SO_2Cl_2 forms HCl, carbon, S, and SO_2.—8. On passing through a *red-hot tube* it yields thiophene.—9. *Chlorine* forms chlorinated products by substitution (Riche, *A.* 92, 358).—10. *Bromine* forms crystalline Et_2SBr_2, whence KI gives oily Et_2SI_2, which is reconverted by $ZnEt_2$ into Et_2S (Rathke, *A.* 152, 214).

Reference.—DI-CHLORO-DI-ETHYL SULPHIDE.

Combinations.—Et_2SHgCl_2. [90°]. Formed as a crystalline pp. by shaking aqueous $HgCl_2$ with Et_2S or its alcoholic solution. Monoclinic prisms (from ether or MeOH) (Loir, *A.* 87, 369).—$(Et_2S)_2PtCl_4$. [108°]. Yellow needles (Loir, *A. Ch.* [3] 39, 441).—$(Et_2S)_2PtCl_2$. [81°]. Formed by shaking Et_2S (1 mol.) with potassium platinous chloride (2 mols.). Short, bright-yellow prisms. Almost insol. water, m. sol. alcohol, sl. sol. ether, v. e. sol. $CHCl_3$. Changed by shaking with water and Et_2S into an isomeride [100°] crystallising in thin tables (Blomstrand, *J. pr.* [2] 27, 190).—$Et_2SPbSO_4$7aq: large crystals; v. e. sol. water.—Et_2SHgI_2. [110°] (Loir, *A.* 107, 234).—Et_2STiCl_4.—$(Et_2S)_2TiCl_4$ (Demarçay, *Bl.* [2] 20, 132).

Methylo-compounds Et_2SMeI. *Methyl-di-ethyl-sulphine iodide.* Formed as a syrup when Et_2S and MeI are heated together with a little water (Krüger, *J. pr.* [2] 14, 195). Moist AgCl gives syrupy Et_2SMeCl. The **hydroxide** is a powerful base. The **nitrate** and **sulphate** crystallise in long deliquescent needles.—$(Et_2SMeCl)_2PtCl_4$: [214°]; pale-red monoclinic crystals; sl. sol. cold water, insol. alcohol and ether. Crystallises from water in cubes, octahedra, and tetrahedra.—$Et_2SMeAuCl_4$: [192°]; long pale-yellow needles; v. sol. alcohol, ether, and hot water. — $Et_2SMeCl(HgCl_2)_6$: [198°]; transparent prisms (from hot water).—$Et_2SMeCyHgI_2$: [115°]; formed by mixing cold solutions of Et_2MeSI, HI, and $HgCy_2$. H_2S in presence of water gives black HgS; on continuing the action of the gas it changes to red HgS (difference from $SEt_3Cl(HgCl_2)_4$).

Isomerides of the Methylo-compounds EtMeSEtI. From EtSMe and EtI (Krüger, *J. pr.* [2] 14, 207). Very deliquescent needles. The chloride is a syrup, the nitrate and sulphate are deliquescent.—$(EtMeSEtCl)_2PtCl_4$: [186°] (K.); [205°] (N. a. S.); prisms of cubic system (from water); insol. ether and alcohol (Nasini a. Scala, *G.* 18, 62). By repeated recrystallisation it is changed into its isomeride.—$EtMeSEtAuCl_4$: [178°]; pale-yellow crystalline powder; v. sol. hot water, alcohol, and ether.—$EtMeSEtCl(HgCl_2)_2$: [112°]; white crystalline pp. Crystallises from water in trimetric plates.—$EtMeSEtCyHgI_2$: [98°]; amber-yellow pp.; insol. water, alcohol, and ether. When strongly heated it yields HgI_2, a carbamine and a sulphide. Both Et_2SMeI and its isomeride EtMeSEtI give with AgOBz syrupy benzoates, which, when heated to 115°, yield methyl benzoate (Crum Brown a. Blaikie, *Pr. E.* 10, 254).

Ethylo-iodide Et_3SI. *Tri-ethyl-sulphine iodide.* From Et_2S and EtI (Oefele, *A.* 132, 82; *C. J.* 17, 106; Lukaschewicz, *Z.* [2] 4, 643). Formed also by the action of HI on Et_2S or EtSH; and by treating mercaptan with EtI (Cahours, *A.* 135, 352; 136, 151). Trimetric plates; v. e. sol. water. Decomposed on distillation into Et_2S and EtI. Moist Ag_2O converts it into a deliquescent hydroxide Et_3SOH. This hydroxide is strongly alkaline; it absorbs CO_2 from the air, ppts. metallic salts, expels NH_3 from its salts, and turns red litmus blue. It forms the following salts:—Et_3SCl: deliquescent needles (from water) volatile with steam. — $(Et_3SCl)_2PtCl_4$: monoclinic prisms, $a:b:c = ·675:1:1·107$; $\beta = 55° 6'$ (Dehn, *A. Suppl.* 4, 92). S. 3·3 at 20·7°.—$Et_3SCl(HgCl_2)_4$. S. 1·5 at 20°.—SEt_3AuCl_4: long golden needles; sl. sol. cold water.—$Et_3SNO_3AgNO_3$.—$(Et_3S)_2SO_4$: indistinct crystalline aggregates.—SEt_3Br: needles; v. e. sol. water, sl. sol. alcohol, insol. ether (*cf.* Otto a. Rössing, *B.* 19, 1839). The ethylo-iodide also forms the following combinations with metallic salt: SEt_3IHgI_2.—SEt_3ITlI_2 (Jörgensen, *J. pr.* [2] 6, 82).—$(SEt_3I)_3(BiI_3)_2$ (Kraut, *A.* 210, 321).—SEt_3IBiI_3.—$(SEt_3I)_2(BiI_3)_3$9aq.

Ethylo-cyanide SEt_3Cy. Formed by digesting SEt_3I with KCy at 100° (Gauhe, *Z.* [2] 4, 622). Deliquescent needles. Resolved by heating with acids or alkalis into Et_2S, propionic acid, and NH_3. A crystalline compound $SEt_3CyAgCy$ is obtained by digesting Et_3SI with alcohol and AgCy at 90°. It is decomposed by heat into SEt_3Cy and AgCy (Patein, *C. R.* 106, 861).

Di-ethyl di-sulphide Et_2S_2. Mol. w. 122. (153° cor.). S.G. $\frac{20}{4}$ ·9927. V.D. 4·27 (calc. 4·23).

Formation.—1. By distilling $KEtSO_4$ with a concentrated aqueous solution of K_2S_2 (Zeise, *P.* 31, 371; Pyr. Morin, *P.* 48, 483; *A.* 32, 267; Löwig, *P.* 27, 550; 49, 326; Cahours, *A. Ch.* [3] 18, 268; *A.* 61, 98; Muspratt, *C. J.* 3, 19).—2. By distilling oxalic ether with K_2S_2.—3. By treating an aqueous solution of sodium mercaptide with iodine (Kekulé a. Linnemann, *A.* 123, 279).—4. By treating mercaptan with conc. H_2SO_4, sulphurous acid being given off (Erlenmeyer a. Lisenko, *Z.* 1861, 660).—5. By heating mercaptan with sulphur for six hours at 150° (M. Müller, *J. pr.* [2] 4, 39).—6. By heating NaSEt (8 g.) with alcohol (10 g.) and sulphur (1·5 g.) at 100° (Böttger, *A.* 223, 348): $2NaSEt + S_2 = Et_2S_2 + Na_2S_2$.—7. From mercaptan and SO_2Cl_2 (Courant a. Richter, *B.* 18, 3178).

Properties.—Colourless oil; sol. alcohol and ether. It first floats upon water, but after a while it sinks, probably from absorption of water. Neutral to test papers. It has an alliaceous odour, and is poisonous. It is very inflammable, and burns with a blue flame. It is attacked by Cl and Br. With HgO it slowly forms a yellow mass. Its alcoholic solutions are ppd. by $HgCl_2$ and by $Pb(OAc)_2$.

Reactions.—1. Dilute *nitric acid* oxidises it to ethane thiosulphonic ether $C_2H_5.SO_2SEt$.—2. Cold H_2SO_4 does not dissolve it; on warming it gives off SO_2.—3. Heated in a sealed tube with EtI it gives SEt_3I and iodine (Saytzeff, *Z.* [2] 6, 109).—4. Carbonised by S_2Cl_2, $SOCl_2$, $ClSO_3H$, and SO_2Cl_2.

Di-ethyl trisulphide Et_2S_3. Obtained, together with Et_2S_2, by distilling $KEtSO_4$ with P_2S_5 (Cahours). Formed also by heating Et_2S_2 with sulphur. Heavy yellow oil, volatile with steam. It cannot be distilled undecomposed. Mercury removes one-third of its sulphur. Copper turnings at 150° do so also. When suspended in water, and oxidised by fuming HNO_3 there is formed H_2SO_4 and $EtSO_3H$. Moist Ag_2O gives $EtSO_3H$ and Ag_2S (Müller).

Di-ethyl tetrasulphide Et_2S_4. Formed by treating mercaptan with S_2Cl_2 in CS_2 solution (Claesson, *J. pr.* [2] 15, 214). Oil with disgusting smell. Split up by distillation in steam into Et_2S_3 and sulphur.

Di-ethyl pentasulphide Et_2S_5. A semi-solid mass got by heating the preceding with sulphur at 150°.

TRI-ETHYL-SULPHINE COMPOUNDS *v. supra.*

ETHYL-SULPHINIC ACID *v.* ETHANE SULPHINIC ACID.

ETHYL SULPHITES.

Mono-ethyl sulphite. The potassium salt KO.SO.OEt is formed when di-ethyl sulphite is treated with cold aqueous KOH (Warlitz, *A.* 143, 75). Scales (from alcohol); very unstable.

Chloride EtO.SO.Cl. (122°). From $(EtO)_2SO$ and PCl_5 (Michaelis a. Wagner, *B.* 7, 1073). Formed in small quantity by passing HCl into alcohol saturated with SO_2 and heating the product in a sealed tube at 100°. Slightly fuming liquid. Readily decomposed by water into HCl, alcohol, and SO_2. Not attacked by PCl_5 at 120°, but at 180° it yields $SOCl_2$, $POCl_3$ and EtCl.

Di-ethyl sulphite $C_4H_{10}SO_3$ *i.e.* $(EtO)_2SO$. (161°). S.G. ^{16} 1·085. V.D. 4·78.

Formation.—1. By the action of absolute alcohol on S_2Cl_2. The reaction perhaps takes place thus: $S_2Cl_2 + HOEt = SOCl_2 + HSEt$; and $SOCl_2 + 2HOEt = SO(OEt)_2 + 2HCl$, but EtCl, HCl, and sulphur are also formed (Carius, *A.* 106, 291; 110, 221; 111, 93; *J. pr.* [2] 2, 279; Ebelmen a. Bouquet, *A. Ch.* [3] 17, 66; Warlitz, *A.* 143, 74).—2. By adding alcohol drop by drop to $SOCl_2$ (Carius).

Properties.—Colourless liquid, smelling somewhat like mint. Miscible with alcohol and ether, but insol. water. Slowly decomposed by water. Aqueous alkalis and Na_2CO_3 quickly decompose it into alkaline sulphite and alcohol. Alcoholic KHO gives a pp. of EtO.SO.OK. Alcoholic NH_3 at 130° gives ethylamine and $(NH_4)_2SO_3$. Ethylamine gives $NHEt_2$ and $(NH_3Et)_2SO_3$. PCl_5 forms EtO.SOCl, which, however, on keeping, or on distilling, rapidly splits up into EtCl and SO_2 (Geuther, *A.* 224, 223). Chlorine attacks it strongly, and in bright sunshine forms C_2Cl_6, $CCl_3.COCl$, and SO_2Cl_2. $SOCl_2$ at 120° gives SO_2 and EtCl. Diethyl sulphite is split up at 200° into SO_2 and ether (Prinz, *A.* 223, 374).

Isomeride *v. Ethyl ether* of ETHANE SULPHONIC ACID.

ETHYL SULPHOCYANIDE C_3H_5NS *i.e.* EtS.Cy. (146° cor.). S.G. $\frac{0}{}$ 1·033; $\frac{23}{}$ 1·002 (Buff, *Z.* [2] 4, 730); $\frac{4}{4}$ 1·071 (Nasini a. Scala, *G.* 17, 66); $\frac{16}{}$ 1·020. V.D. 3·02. R_∞ 41·4 (N. a. S.).

Formation (Cahours, *A. Ch.* [3] 18, 264; Löwig, *P.* 67, 101; Muspratt, *A.* 65, 253).—1. By saturating a concentrated solution of potassium sulphocyanide with EtCl; the product is diluted with an equal bulk of water and distilled, the distillate mixed with ether, diluted with water, and the ethereal solution dried over $CaCl_2$ and rectified.—2. From EtI and silver sulphocyanide (Meyer a. Wurster, *B.* 6, 965).—3. By distilling equal parts of calcium ethyl sulphate with potassium sulphocyanide, both in concentrated solution.

Properties.—Mobile colourless oil, having a taste of anise and a pungent odour resembling mercaptan. Insol. water, miscible with alcohol and ether. Its alcoholic solution does not ppt. solutions of metallic salts.

Reactions.—1. *Nitric acid* oxidises it to ethane sulphonic acid.—2. $KClO_3$ and HCl attack it with great violence forming ethane sulphonic acid.—3. *Chlorine* forms chloride of cyanogen Cy_3Cl_3, and a liquid $C_2H_3SCl_3$ (135°) (James, *J. pr.* [2] 30, 316).—4. Aqueous KOH at 100° gives Et_2S_2, potassium cyanate, and KCy (Brüning, *A.* 104, 193).—5. Boiling alcoholic KOH gives off NH_3 and Et_2S_2.—6. Alcoholic K_2S forms Et_2S and potassium sulphocyanide.—7. Dry *ammonia* appears to form a little ethyl-thio-urea. Aqueous ammonia (S.G. ·880) forms black uncrystallisable products. Dilute aqueous NH_3 forms NH_4Cy, urea, and Et_2S_2 (Jeanjean, *C. R.* 55, 330; Kremer, *J. pr.* 73, 365).—8. PEt_3 at 100° forms Et_3PS and Et_4PCy (Hofmann, *B.* 4, 611; *A. Suppl.* 1, 53).—9. Dry H_2S gives di-thio-carbamic ether $NH_2.CS_2Et$.—10. *Thio-acetic acid* gives $NHAc.CS_2Et$.—11. MeI at 105° gives Me_3SI and other products (Dehn, *A. Suppl.* 4, 107).—12. HBr forms a compound $EtSCyH_2Br_2$ (Henry, *J.* 1868, 652).

Reference.—CHLORO-ETHYL SULPHOCYANIDE.

DI-ETHYL-SULPHONE $C_4H_{10}SO_2$ *i.e.* Et_2SO_2. *Ethane sulphinic ether.* Mol. w. 122. [70°]. (248°). S. 16 at 16°. R_∞ 46·60 (in a 4·24 p.c. aqueous solution) (Kanonnikoff).

Formation.—1. By oxidising di-ethyl sulphide with HNO_3 in sealed tubes at 100°.—2. By oxidising di-ethyl sulphide with a solution (1:30) of $KMnO_4$.—3. From sodium ethane sulphinate and EtBr (Otto, *B.* 13, 1278).—4. By heating its α-carboxylic acid to 200° (Otto, *B.* 21, 994).—5. From lead ethide and SO_2 (Frankland a. Lawrance, *C. J.* 35, 245).—6. By the dry distillation of its dicarboxylic acid $SO_2(CHMe.CO_2H)_2$ (Lovén, *B.* 17, 2823).

Properties.—Trimetric tables (from hot water or alcohol). Does not reduce $KMnO_4$; is not reduced by Zn and H_2SO_4 (differences from di-ethyl sulphoxide, Beckmann, *J. pr.* [2] 17, 452). Not attacked by PCl_5, chlorine, or $ZnEt_2$. ICl_3 at 150° gives $C_4H_9ClSO_2$ and other products (Spring a. Winssinger, *B.* 15, 446).

ETHYL-SULPHONO-ACETIC ACID *v.* METHYL-ETHYL SULPHONE CARBOXYLIC ACID.

DI-ETHYL-SULPHONE α-CARBOXYLIC ACID $EtSO_2CHMe.CO_2H$. *α-Ethyl-sulphono-propionic acid.* The ethyl ether is obtained by boiling the ethyl ether of α-chloropropionic acid with sodium ethane sulphinate (Otto, *B.* 21, 994). The free acid is a yellowish oil, miscible with alcohol and water. Decomposed on heating into di-ethyl-sulphone and CO_2. The Na salt is a gum.

Di-ethyl-sulphone β-carboxylic acid $Et.SO_2.CH_2.CH_2.CO_2H$. '*β-Ethyl-sulphono-propionic acid.* [112°]. The ethyl ether is obtained by the action of β-iodopropionic acid on sodium ethane sulphinate in an alcoholic solution (Otto, 21, 995). The free acid forms plates, v. e. sol. alcohol and ether. At 200° it gives SO_2 and propionic acid. The Na salt crystallises from alcohol in plates, and is v. e. sol. water.

Di-ethyl-sulphone di-carboxylic acid $O_2S(C_2H_4.CO_2H)_2$. *Sulpho-di-propionic acid.* [156°].

Formation.—1. By oxidation of thio-di-α-lactic acid $S(C_2H_4.CO_2H)_2$ with $KMnO_4$.—2. By the action of methyl iodide and sodium ethylate upon di-methyl-sulphone di-carboxylic ether (Lovén, *B.* 17, 2822).

Properties.—Four-sided tables. V. sol. water, alcohol, and ether. On heating it loses CO_2, forming di-ethyl-sulphone.

ETHYL-SULPHONE-ETHYLAMIDE *v. Ethylamide* of ETHANE SULPHONIC ACID.

DI-ETHYL-SULPHONE-DI-METHYL-METHANE *v.* DI-ETHYL PROPYLIDENE DI-SULPHONE.

ETHYL-SULPHONO-PROPIONIC ACID *v.* DI-ETHYL-SULPHONE CARBOXYLIC ACID.

ETHYL SULPHO-UREA *v.* ETHYL-THIO-UREA.

DI-ETHYL SULPHOXIDE Et_2SO. *Ethyl oxysulphide.* Formed by heating Et_2S with dilute nitric acid (S.G. 1·2). Thick syrup, v. sol. water, Cannot be distilled. Reduced by zinc and H_2SO_4 to Et_2S (Saytzeff, *A.* 144, 153). Chlorine gives EtCl and chlorinated derivatives of ethane sulphonic acid. Chlorine passed into its aqueous solution forms HCl, EtCl, and $EtSO_2Cl$ (Spring a. Winssinger, *B.* 15, 447).

Di-ethyl-di-sulphoxide *v. Ethyl ether* of ETHANE THIOSULPHONIC ACID.

ETHYL SULPHYDRATE *v.* MERCAPTAN.

ETHYL TARTRONIC ACID *v.* OXY-ETHYL-MALONIC ACID.

ETHYL-TAURINE *v.* ETHYL-AMIDO-ETHANE SULPHONIC ACID.

ETHYL-TELLURIDE Et_2Te. (98°) (W.; H.); (138°) (M. a. M.). From K_2Te and $KEtSO_4$ (Wöhler, *A.* 35, 111; 84, 69; Heeren, *C. C.* 1861, 916). Reddish-yellow liquid with disgusting odour, v. sl. sol. water. Oxidised by air.

Chloride Et_2TeCl_2. Prepared by treating Et_2Te with HNO_3, dissolving the resulting crystalline nitrate in water, and ppg. by HCl. Oil. *Reactions.*—1. Aqueous NH_3 gives $(Et_2Te)_2Cl_2O$, crystallising in six-sided prisms, whence Ag_2SO_4 gives crystalline $(Et_2Te)_2H_2SO_4$.—2. Ag_2O forms an unstable alkaline oxide, which is reduced by SO_2 to Et_2Te.

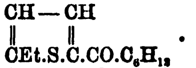
Ethylo-chloride Et_3TeCl. [174°]. From $ZnEt_2$ and $TeCl_4$ in ether (Marquardt a. Michaelis, *B.* 21, 2042). Deliquescent. Excess of $ZnEt_2$ at 105° forms $TeEt_4$ and butane.

Ethylo-iodide Et_3TeI. [92°]. From Et_2Te and EtI at 50° (Becker, *A.* 180, 263; Cahours, *A. Ch.* [5] 10, 50). Monoclinic crystals. Gives with Ag_2O an unstable alkaline base.

DI-ETHYL-THETINE $_{\times}C_6H_{14}SO_3$ *i.e.* $Et_2S(OH).CH_2.CO_2H$. Obtained by adding Ag_2O to an aqueous solution of its hydrobromide (Letts, *Tr. E.* 28, 584). Thick syrup.

Salts.—$Et_2SBr.CH_2.CO_2H$. Formed by shaking Et_2S with bromo-acetic acid, and allowing to stand for a few days. Colourless prisms, sol. water and alcohol, insol. ether. It forms a lead salt $Et_2SBr.CH_2.CO_2PbBrPbBr_2$ which crystallises either in narrow plates or in needles, sl. sol. cold, v. sol. hot, water. Strong nitric acid oxidises di-ethyl-thetine to ethane sulphonic acid.—$^{\times}Et_2SCl.CH_2.CO_2H$: syrupy liquid.—$(Et_2SCl.CH_2.CO_2H)_2PtCl_4$: large dark-orange crystals.—$^{\times}(SEt_2.CH_2.CO_2H)_2SO_4$: syrup.

ETHYL-THIËNYL HEXYL KETONE $C_{12}H_{20}SO$ *i.e.*



$$\begin{array}{l}\;CH - CH\\ \|\qquad\;\;\|\\ CEt.S.C.CO.C_6H_{13}\end{array}$$

. (330° cor.). From ethyl-thiophene, heptoyl chloride, and $AlCl_3$ (Schleicher, *B.* 19, 660). Yellow oil of aromatic odour. Yields on oxidation hexoic acid and thiophene *aa*-dicarboxylic acid. By heating with H_2SO_4 it gives heptoic and ethyl-thiophene sulphonic and disulphonic acids.

Oxim.—$C_4SH_2Et.C(NOH).C_6H_{13}$. [39°]. Crystalline.

(β)-ETHYL-THIËNYL METHYL KETONE $C_4SH_2Et.CO.CH_3$. *Aceto-ethyl-thiënone.* (249° cor.). S.G. $\frac{20}{}$ ·096. Formed by the action of acetyl chloride upon (*a*)-ethyl-thiophene in presence of Al_2Cl_6 (Schleicher, *B.* 18, 3020; 19, 660). Liquid. By alkaline $KMnO_4$ it is oxidised to thiophene di-carboxylic acid.

Oxim $C_4SH_2Et.C(NOH).CH_3$: [110°]; white crystals.

Phenyl-hydrazide. [68°]. Needles.

Nitro-derivative $C_4SHEt(NO_2)(CO.CH_3)$: [71°]; white needles.

Di-ethyl-thiënyl methyl ketone $C_4SHEt_2.CO.CH_3$. *Acetodiethylthiënone.* (250°). A mixture of di-ethyl-thiophene (1 g.), AcCl (·6 g.), petroleum-ether (5 g.) is slowly dropped into petroleum-ether (30 g.), in which $AlCl_3$ (2 g.) is suspended. The product is treated with cold water and distilled (Muhlert, *B.* 19, 635). Oil.

Oxim $C_4SHEt_2.C(NOH).CH_3$. Oil.

ETHYL-(*a*)-THIOCARBAMIC ACID. *Ethyl ether* $NHEt.CO.SEt$. (204°-208°). From mercaptan and cyanic ether (Hofmann, *B.* 2, 118). Heavy oil. Decomposed by acids or alkalis into mercaptan, CO_2, and ethylamine.

Benzoyl derivative ? $NBzEt.CO.SH$. [74°]. From BzCl and potassium sulphocyanide in alcoholic solution (Lössner, *J. pr.* [2] 10, 235). On pouring the product into water the acid separates as hard sulphur-yellow prisms, v. sl. sol. water, v. sol. alcohol and ether. Resolved by heat into mercaptan, benzonitrile, and CO_2. Hot aqueous KOH gives KOBz, potassium sulphide, potassium carbonate, and potassium sulphocyanide.—$NBzEt.CO.SK$: small needles (from alcohol), v. sol. water, sl. sol. alcohol and ether.—AgA': flocculent pp. turns black on heating.—EtA'. From the K salt and EtBr. Heavy non-volatile oil. At 105° it forms crystals [129°].—$C_5H_{11}A'$? small prisms, sol. water and alcohol; formed from isoamyl alcohol and benzoyl sulphocyanide (Miquel, *A. Ch.* [5] 11, 330).—C_6H_5A': [93°]; minute needles (from dilute alcohol); insol. water, v. sol. alcohol and ether.

Ethyl-(β)-thiocarbamic acid. *Ethyl ether* $NHEt.CS.OEt$. *Ethyl-urethane.* (204°-208°). From ethyl thiocarbimide and alcohol by heating for several hours at 110° (Hofmann, *B.* 2, 117). Formed also by treating ethyl thio-carbimide with alcoholic NaOH. Oil, smelling of garlic. Split up by alkalis or dilute acids into ethylamine, H_2S, alcohol, and CO_2. Conc. H_2SO_4 gives off COS.

Ethyl-di-thio-carbamic acid $NHEt.CS.SH$. The ethylamine salt is formed by adding CS_2 slowly to an ethereal solution of ethylamine at −18° (Hofmann, *B.* 1, 25; Rudneff, *J. R.* 10, 188; *B.* 11, 987; *Bn.* 1, 998); the free acid is ppd. on adding the calculated quantity of HCl to a solution of this salt. It is crystalline. It is decomposed by excess of HCl into CS_2 and ethylamine.

Salts.—The silver salt is a white pp. decomposed by boiling water into silver sulphide and ethyl thiocarbimide.—Ethylamine salt $NHEt.CS.SNH_3Et$. [103°]. Six-sided tables (from alcohol), v. sol. water and alcohol, m. sol. ether. On boiling the alcoholic solution di-ethyl-thio-urea is formed. Iodine attacks its alcoholic solution forming di-ethyl-thio-urea, CS_2, ethyl thiocarbimide, NH_2Et, and sulphur.

Ethyl ether EtA'. *Di-ethyl-xanthamide.* Prepared by digesting mercaptan with ethyl-thiocarbimide at 120° for several hours (Hofmann, *Z.* [2] 5, 268). Heavy oil. Decomposed by distillation.

Di-ethyl-di-thio-carbamic acid. Diethylamine salt $NEt_2.CS.S.NH_2Et_2$. From CS_2 and diethylamine (Grodzki, *B.* 14, 2754). Not decomposed at 110°. Split up by iodine into diethylamine and $C_{10}H_{20}N_2S_4$ or $(NEt_2.CS)_2S_2$ [70°] which may be crystallised from alcohol.

ETHYL-THIO-CARBAMINE-CYAMIDE *v.* CARBIMIDO-ETHYL-THIO-UREA.

ETHYL-THIO-CARBAMINE-METHYL CYAMIDE *v.* METHYL-CARBIMIDO-ETHYL-THIO-UREA.

ETHYL-THIOCARBIMIDE C_3H_5NS *i.e.* EtN.CS. *Ethyl mustard oil.* Mol. w. 87. (133°). V.D. 3·03 (calc. 3·02). S.G. $^{\underline{0}}$ 1·019; $^{\underline{22}}$ ·997 (Buff, *Z.* [2] 4, 730); $\frac{4}{4}$ ·995 (Nasini a. Scala, *G.* 17, 66). R_∞ 43·35.

Formation.—1. By heating cyanic ether with P_2S_5 (Michael a. Palmer, *Am.* 6, 260).—2. By adding an aqueous solution of ethylamine to $CSCl_2$ (Rathke, *A.* 167, 218).—3. By distilling di-ethyl-thio-urea with P_2O_5 or dry HCl (Hofmann, *B.* 1, 26).—4. By distilling ethylamine ethyl-di-thio-carbamate (from CS_2 and NH_2Et) with aqueous silver nitrate, or, better, $HgCl_2$. An excess of $AgNO_3$ must be avoided, or some of the EtNCS will be changed into EtNCO. It is unnecessary to use pure ethylamine, the crude product of the action of alcoholic NH_3 on EtI answers just as well.—5. Formed in small quantity, together with ethyl sulphocyanide and other products, by heating mercuric sulphocyanide with EtI at 180° (Michael, *Am.* 1, 417).

Properties.—Pungent liquid, inflames the tongue.

Reactions.—1. It unites directly with *ammonia* and primary *amines* forming ethyl- and ethyl-alkyl- thio-ureas.—2. Digested for some hours at 110° with *alcohol* it forms ethyl-(β)-thio-carbamic ether.—3. *Mercaptan* at 120° gives ethyl-di-thio-carbamic ether.—4. When *chlorine* is passed through a cooled mixture of equal volumes of ethyl thiocarbimide and dry ether there is formed a powder which by treatment with aqueous NaOH is converted into $(EtNCS)_2O$ [42°]. This oxide of ethyl thiocarbimide crystallises from alcohol in splendid colourless tablets and prisms, insol. water. On treatment with ammonium sulphide sulphur separates and the filtrate deposits crystals [c. 60°] (Sell, *B.* 6, 322).—5. Ethyl thiocarbimide (1 mol.) warmed with aldehyde-ammonia (2 mols.) and alcohol at 100° forms silvery needles of $C_{14}H_{31}N_5S_2O_2$ [119°], v. sol. alcohol, ether, and hot water. Alkalis and dilute acids give off aldehyde, NH_3, ethylamine, &c.

ETHYL THIOCARBONATES. *Sulphocarbonic ethers.*

Mono-ethyl-(α)-thiocarbonate. Salts.—EtO.CO.SK. Formed by the action of alcoholic KOH or KSH on $CS(OEt)_2$, or of KOH on EtO.CS.SEt (Debus, *A.* 75, 130, 136, 142; 82, 253). Formed also by passing CO_2 into an alcoholic solution of KSEt (Chancel, *C. R.* 32, 642). Also from COS and alcoholic KOH (Bender, *A.* 148, 137). Long needles or prisms; v. sol. water and alcohol, insol. ether, not deliquescent. The aqueous solution decomposes on boiling into Et_2CO_3, mercaptan, Et_2S, and alcohol. The dry salt decomposes at 170° into COS, Et_2S, and K_2CO_3. On adding acids to its aqueous solution COS and alcohol are formed. By adding iodine to its alcoholic solution there is formed EtO.CO.S.S.CO.OEt, a heavy oil, which is decomposed by alcoholic KOH giving EtO.CO.SK, sulphur, and K_2S. When NH_3 is passed into its alcoholic solution sulphur is deposited, while Et_2S and allophanic ether remain in solution (Chancel, *C. R.* 32, 644; Debus, *A.* 75, 142).—$(EtO.CO.S)_2Zn$: m. sol. water and alcohol.—$(EtO.CO.S)_2Pb$: crystalline powder, insol. water, sl. sol. alcohol.—EtO.CO.SAg: unstable sticky mass, insol. water.—$(EtO.CO.S)_2Cu\frac{1}{3}Cu_2S$ Obtained by adding cupric sulphate to a solution of the K salt until the milky pp. first formed becomes yellow. This is washed with ether. It is a yellow amorphous powder.

Di-ethyl (α)-thiocarbonate EtO.CO.SEt. (156°). S.G. $^{\underline{15}}$ 1·0285. R_∞ 34·09 (Nasini, *G.* 13, 302). From the K salt and EtBr in alcohol (Salomon, *J. pr.* [2] 6, 438). Also from NaSEt and $ClCO_2Et$. Liquid with characteristic smell. Split up by water at 160° into mercaptan, CO_2, and alcohol. Alcoholic NH_3 gives mercaptan and $EtO.CO.NH_2$. Alcoholic KOH gives mercaptan, alcohol, and potassium carbonate.

Amide $EtS.CO.NH_2$. *Isothiocarbamic ether. Isothiourethane.* [102°] (P.); [108°] (F.).

Formation.—1. By passing gaseous HCl into an alcoholic solution of ethyl sulphocyanide (Pinner, *B.* 14, 1082).—2. From HCl and alcoholic potassium sulphocyanide (Blankenhorn, *J. pr.* [2] 16, 375).—3. From ClCO.SEt and NH_3 (Salomon, *J. pr.* [2] 7, 256).—4. From $NH_2.CO.SNH_4$ and EtBr (Fleischer, *B.* 9, 991).—5. In small quantity from $CO(SEt)_2$ and NH_3 (Salomon a. Conrad, *J. pr.* [2] 10, 32).

Properties.—Plates, may be sublimed; sl. sol. water, v. sol. alcohol. In a sealed tube at 150° it splits up into mercaptan and cyanuric acid. Alcoholic NH_3 gives urea and mercaptan. Alcoholic KOH gives CO_2, ammonia, and mercaptan. P_2O_5 gives ethyl sulphocyanide. $HgCl_2$, $CuSO_4$, and $AgNO_3$ give pps.

Di-ethyl ethylene (α)-di-thio-di-carbonate $(EtO.CO.S)_2C_2H_4$. From EtO.CO.SK and alcoholic ethylene bromide (Welde, *J. pr.* [2] 15, 52). Thick oil with unpleasant odour. Cannot be distilled. Alcoholic NH_3 gives in the cold $C_2H_4(SH)_2$ and carbamic ether. Alcoholic KOH gives in the cold EtO.CO.OK and $C_2H_4(SH)_2$.

Ethyl isobutyl (α)-thiocarbonate $EtO.CO.SC_4H_9$. (192°). S.G. $^{\underline{10}}$ ·994. From $ClCO_2Et$ and $NaSC_4H_9$ (Mylius, *B.* 6, 313). Alcoholic NH_3 converts it into HSC_4H_9 and $EtO.CO.NH_2$. Alcoholic KOH or KSH forms C_4H_9SH, alcohol, and CO_2.

Isobutyl ethyl (α)-thiocarbonate $C_4H_9O.CO.SEt$. (193°). S.G. $^{\underline{10}}$ ·994. From $Cl.CO_2C_4H_9$ and NaSEt (M.). Liquid, smelling like mercaptan. Alcoholic NH_3 gives mercaptan and $C_4H_9O.CO.NH_2$. Warm alcoholic KOH gives EtSH, isobutyl alcohol, and CO_2.

Ethyl-isoamyl thiocarbonate $CO(OEt)(SC_5H_{11})$. From $Cl.CO.S.C_5H_{11}$ and NaOEt. A liquid (Schöne, *J. pr.* [2] 32, 245).

Reactions.—1. Alcoholic NH_3 reacts according to the equation $CO(S.C_5H_{11})(OEt) + NH_3 = HSC_5H_{11} + CO(NH_2)(OEt)$.—2. Alcoholic KOH reacts thus: $CO(SC_5H_{11})(OEt) + 2KOH = HSC_5H_{11} + HOEt + K_2CO_3$.

Ethyl (β)-thio-carbonic acid.

Chloride EtO.CSCl. (136°). Colourless pungent oil; formed in small quantity by the action of alcohol on $CSCl_2$. Converted by NH_3 into the amide (Klason, *B.* 20, 2385).

Amide $EtO.CS.NH_2$. *Xanthogenamide.* [38°] (Salomon, *J. pr.* [2] 8, 115). Formed by the action of alcoholic NH_3 on EtO.CS.SEt (Debus, *A.* 75, 128), on EtO.CS.Cl (Klason), on EtO.CS.SMe (Chancel, *J.* 1851, 513), or on $(EtO.CS)_2S_2$. Monoclinic pyramids. M. sol. water, v. e. sol. alcohol and ether. Split up by dry distillation into mercaptan, cyanic acid, and cyanuric acid. Alcoholic KOH or baryta form alcohol and a sulphocyanide. P_2O_5 gives ethyl sulphocyanide (Salomon a. Conrad, *J. pr.* [2] 10, 84).

Combinations.—$(C_3H_7NSO)_2Cu_2Cl_2$. Formed by adding $CuSO_4$ to the aqueous solution and decomposing the pp. with HCl. Small rhombohedra (from alcohol); v. sl. sol. water.—$(C_3H_7NSO)_4Cu_2Cl_2$.—$(C_3H_7NSO)_6Cu_2Cl_2$.—$(C_3H_7NSO)_8Cu_2Cl_2$.—$(C_3H_7NSO)_2CuI$.—$(C_3H_7NSO)_4CuI$.—$(C_3H_7NSO)_2Cu_2(SCy)_2$.—$(C_3H_7NSO)_4 3Cu_2(SCy)_2$.—$C_3H_7NSO5Cu_2(SCy)_2$.—$(C_3H_7NSO)_4Pt_2Cl_6$ (Debus).

Di-ethyl (β)-thiocarbonate EtO.CS.OEt. (162°). S.G. $^{\underline{1}}$ 1·032. R_∞ 34·51 (Nasini, *G.* 13, 303).

Formation.—1. By the dry distillation of EtO.CS.S.S.CS.OEt, the other products being CS_2 and EtO.CS.SEt (Debus, *A.* 75, 136).—2. From $CSCl_2$ and KOEt (Salomon, *J. pr.* [2] 6, 441).

Properties.—Liquid with pleasant odour. Insol. water, v. sol. alcohol and ether.

Reactions.—1. Alcoholic KHS gives mercaptan and EtO.CO.SK.—2. Alcoholic KOH gives alcohol, EtO.CO.SK, and EtO.CO.OK.—3. Cold alcoholic NH_3 gives NH_4SCy and alcohol.

Mono-ethyl (αβ)-di-thio-carbonate EtO.CS.SH. *Xanthogenic acid. Xanthic acid.*

Formation.—KOH (2 pts.) is dissolved in alcohol (1 pt.), and CS_2 is slowly added until the liquid is no longer alkaline. On cooling to 0° the potassium xanthate separates in colourless needles from which the acid may be obtained by treatment with dilute H_2SO_4 (Zeise, *Sch. J.* 36, 1; 43, 160; *P.* 35, 457; Couerbe, *A. Ch.* [2] 61, 225; Sacc, *A.* 51, 345; Debus, *A.* 72, 1; 75, 121; 82, 253; Desains, *A. Ch.* [3] 20, 496; Hlasiwetz, *A.* 122, 87). Potassium xanthate is also formed by treating xanthic ether with KHS.

Properties.—Colourless heavy oil, with strong odour. It first reddens litmus, then bleaches it. It is very inflammable. At 24° it seems to boil, being split up into CS_2 and alcohol. It expels CO_2 from its salts.

Salts.—The soluble xanthates form a white pp. with lead salts, a yellow pp. with cupric salts (hence the name), and a light-yellow pp. with silver and mercurous salts; the last-mentioned pp. turning black.—KA′. S.G. $^{\underline{21.5}}$ 1·5576 (Clarke, *B.* 11, 1505). S. (alcohol) 20. Prepared as above. Colourless prisms which turn slightly yellow on exposure to air. V. sol. water and alcohol, insol. ether. Its aqueous solution decomposes above 50° into K_2CS_3, alcohol, H_2S, and CO_2. In the dry state it may be heated to 200° without alteration; at a higher temperature it decomposes, leaving a residue of K_2S mixed with charcoal. Hot KOHAq forms EtO.CO.SK. Iodine added to its alcoholic solution gives EtO.CS.S.S.CS.OEt, which is also formed by the action of iodine on lead xanthate (Desains, *A. Ch.* [3] 20, 469; Debus, *A.* 72, 1). This substance [28°] S.G. 1·260 (N. a. S.) forms prisms, v. e. sol. alcohol and ether, insol. water. $(EtO.CS)_2S_2$ is split up on distillation into EtO.CS.SEt, $(EtO)_2CS$, CO, sulphur, and CS_2. Potassium unites with $(EtO.CS)_2S_2$, forming potassium xanthate (Drechsel, *Z.* 1865, 583). Alcoholic NH_3 converts $(EtO.CS)_2S_2$ into xanthamide and ammonium xanthate. Alcoholic KOH gives potassium xanthate, CO_2, and sulphur. Alcoholic KSH also converts $(EtO.CS)_2S_2$ into potassium xanthate, H_2S and S being set free. Aniline converts $(EtO.CS)_2S_2$ into NHPh.CS.OEt and $CS(NHPh)_2$ (Hofmann, *B.* 5, 773). Potassium xanthate is converted by $ClCO_2Et$ into $S(CS.OEt)_2$ [55°]. This body crystallises from alcohol in golden needles, split up by alcoholic NH_3 into $EtO.CS.NH_2$ and H_2S, and by alcoholic KOH into EtO.CO.SK and EtO.CS.SK (Welde, *J. pr.* [2] 15, 45).—NaA′: yellow needles.—NH_4A': colourless needles, resembling urea. V. e. sol. water and alcohol.—$BaA'_2 2aq$: from alcohol, BaO, and CS_2. Very unstable laminæ; sol. water.—*CaA'_2: gummy mass.—AsA'_3. Prepared by dropping a solution of $AsCl_3$ in CS_2 into alcoholic NaOEt, with cooling. The liquid is filtered from NaCl, and allowed to evaporate spontaneously (Hlasiwetz). Colourless monoclinic tables (from CS_2). V. e. sol. CS_2. Decomposed by heat, leaving As_2S_3. Decomposed by warm aqueous HCl.—SbA'_3. Prepared in the same way as the preceding xanthate, using $SbCl_3$. Large lemon-yellow triclinic crystals.—BiA'_3: golden-yellow laminæ and tables.—CrA'_3: shining dark-blue crystals; m. sol. CS_2, forming a violet-blue solution.—CoA'_2: large black crystals, m. sol. CS_2 forming a dark grass-green solution (H.). Insol. NH_3 (Phipson, *C. R.* 84, 1459).—NiA'_2: large black monoclinic tables, m. sol. CS_2 forming a yellowish-green solution (H.). Sol. NH_3Aq.—HgA'_2. From NaOEt and $HgCl_2$ in CS_2 (H.). Satiny scales, m. sol. CS_2.—SnA'_2. From NaOEt, $SnCl_4$, and CS_2 in the same manner as AsA'_3 (H.). Golden laminæ and tables.—FeA'_3: black monoclinic crystals; its solution in CS_2 is brownish-black (H.).—$Cu_2A'_2$. Potassium xanthate added to a solution of a cupric salt forms at first a brownish-black pp. of cupric xanthate, but this quickly changes to beautiful yellow flocculi of cuprous xanthate. This salt is not sensibly attacked by H_2S, but ammonium sulphide decomposes it immediately. It is decomposed by hot acids. It is insol. water and NH_3, sol. CS_2.—PbA'_2. Prepared by adding CS_2 and lead hydroxide to alcoholic KOH. Colourless silky needles; insol. water and ether, m. sol. boiling alcohol. Slowly decomposed by H_2S, immediately by ammonium sulphide. When boiled with aqueous KOH a pp. of PbS is formed. Cupric sulphate solution poured on the crystals immediately changes them to cuprous xanthate (Debus).—ZnA'_2: granular pp.; sl. sol. water, m. sol. alcohol, v. sol. NH_3Aq (P.).

Chloride and *Amide v. supra.*

Methyl ethyl (αβ)-dithiocarbonate EtO.CS.SMe. *Methyl xanthate.* (179°) (S.); (184°) (C.). S.G. $\frac{4}{4}$ 1·119 (Nasini a. Scala, *G.* 17, 66); $^{\underline{11}}$ 1·123 (C.); $^{\underline{18}}$ 1·129 (S.). R_∞ 65·67. V.D. 4·65. Obtained by distilling $KMeSO_4$ with potassium xanthate (Chancel, *A. Ch.* [3] 35, 468). Also from potassium xanthate and MeI (Salomon, *J. pr.* [2] 8, 116). Pale-yellow oil; sol. alcohol and ether. Alcoholic KOH gives MeSH and xanthamide $EtO.CS.NH_2$.

Di-ethyl (αβ)-di-thio-carbonate EtO.CS.SEt. *Xanthic ether.* Mol. w. 150. (200°). S.G. $\frac{4}{4}$ 1·074 (N. a. S.). R_∞ 70·95.

Formation.—1. From EtO.CS.SK and EtCl (Debus), or EtBr (Salomon, *J. pr.* [2] 6, 445).—

2. By the dry distillation of (EtO.CS)$_2$S$_2$ (Zeise).

Properties.—Pale-yellow oil, smelling like garlic; miscible with alcohol and ether. It dissolves iodine. It is but slightly attacked by potassium. It is not attacked by HCl. Its alcoholic solution gives a white pp. with HgCl$_2$. HgO, PbO, and PbO$_2$ do not act on it.

Reactions.—Alcoholic KSH gives mercaptan and EtO.CS.SK. Alcoholic KOH acts in like manner. NH$_3$ passed into its alcoholic solution forms Et$_2$S, H$_2$S, and EtO.CS.NH$_2$. Aqueous NH$_3$ at 135° forms alcohol, mercaptan, and NH$_4$SCy. Water at 160° gives mercaptan, alcohol, CO$_2$ and H$_2$S (Schmitt a. Glutz, *B.* 1, 168).

Chloride EtS.CSCl. (100° *in vacuo*). S.G. ^{18} 1·1408. From mercaptan and CSCl$_2$ (Klason, *B.* 20, 2385).

Amide EtS.CS.NH$_2$. [42°]. Formed by passing H$_2$S into ethyl sulphocyanide at 100° under extra pressure (Jeanjean, *J.* 1866, 501; Salomon a. Conrad, *J. pr.* [2] 10, 29). Trimetric crystals (from ether) with unpleasant odour. Insol. water, v. e. sol. alcohol and ether. Alcoholic NH$_3$ or KOH gives mercaptan and sulphocyanide. EtI forms crystalline EtS.CS.NH$_2$EtI. HgCl$_2$, AgNO$_3$, and CuSO$_4$ give pps.

Acetyl derivative of the Amide EtS.CS.NHAc. [123°]. Yellow needles; sol. alcohol, ether, and hot water. Boiled with baryta-water it gives mercaptan, barium sulphocyanide, and barium acetate. Formed by the combination of thio-acetic acid with ethyl-sulphocyanide. On dry distillation it is decomposed into these constituents (Chanlaroff, *B.* 15, 1987).

Ethylene ethyl (*αβ*)-di-thiocarbonate (EtO.CS.S)$_2$C$_2$H$_4$. [42°]. From potassium xanthate and alcoholic ethylene bromide (Welde, *J. pr.* [2] 15, 55). Long needles or tables (from ether). Alcoholic NH$_3$ gives EtO.CS.NH$_2$ and C$_2$H$_4$(SH)$_2$.

Ethyl propyl (*αβ*)-di-thiocarbonate EtO.CS.SPr. S.G. $\frac{4}{4}$ 1·050. R$_\infty$ 78·55 (Nasini a. Scala, *G.* 17, 66).

Ethyl isobutyl (*αβ*)-di-thio-carbonate C$_4$H$_9$O.CS.SEt. (228°). S.G. ^{17} 1·003. From C$_4$H$_9$O.CS.SK and EtI (Mylius, *B.* 5, 975).

Di-ethyl-(*αα*)-di-thiocarbonate CO(SEt)$_2$. (197°). S.G. ^{22} 1·084.

Formation.—1. By warming ethyl sulphocyanide with conc. H$_2$SO$_4$ (Schmitt a. Glutz, *B.* 1, 166).—2. From NaSEt and COCl$_2$ (Salomon, *J. pr.* [2] 7, 255).—3. From di-phenyl carbonate and NaSEt (Seifert, *J. pr.* [2] 31, 464).

Properties.—Oil, smelling like garlic. Alcoholic NH$_3$ splits it up into urea and mercaptan. Alcoholic KOH gives KEtCO$_3$ and mercaptan. Water at 160° forms CO$_2$ and mercaptan.

Mono-ethyl tri-thio-carbonate EtS.CS.SH. **Salt.**—KA′. Formed by direct union of CS$_2$ with KSEt (Chancel, *C. R.* 32, 642). Sol. water and alcohol. Its solution gives yellow pps. with salts of Ag, Pb, and Hg; and with CuSO$_4$ a scarlet pp. of the cuprous salt. These pps. decompose when heated, leaving metallic sulphides. The K salt decomposes at 100° into P$_2$S$_5$ and an oil C$_6$H$_{10}$S?

Di-ethyl tri-thio-carbonate EtS.CS.SEt. (240°).

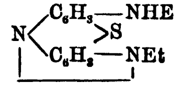
Formation.—1. From K$_2$CS$_3$ or Na$_2$CS$_3$ and EtI or EtCl (Schweitzer, *J. pr.* 32, 254; Debus, *A.* 75, 147; Hüsemann, *A.* 123, 67).—2. By acting on EtI and CS$_2$ with sodium amalgam (Nasini a. Scala, *G.* 17, 236; *cf.* Löwig a. Scholz, *J. pr.* 79, 441).—3. From CSCl$_2$ and NaSEt (Klason, *B.* 20, 2385).

Properties.—Heavy yellow oil, v. sol. alcohol and ether. Has a slightly alliaceous odour. Burns with blue flame. When heated slowly it partially decomposes into Et$_2$S and CS$_2$. Alcoholic KOH gives K$_2$CS$_3$, mercaptan, &c. Alcoholic NH$_3$ at 100° gives mercaptan and ammonium sulphocyanide. Unites with bromine, forming Et$_2$CS$_3$Br$_2$, which crystallises from ether in large six-sided prisms, decomposed by water with liberation of HBr, and by potash with liberation of the original ether (Behrend, *A.* 128, 333). Oxidised by HNO$_3$ to ethane sulphonic acid.

Ethyl-ortho-thio-carbonate C(SEt)$_4$. S.G. 1·01. Formed by treating CCl$_4$ with NaSEt (Claesson, *J. pr.* [2] 15, 212). Oil, with unpleasant odour. Gives off Et$_2$S$_2$ when heated. Volatile with steam. Oxidised by HNO$_3$ to ethane sulphonic acid.

ETHYL THIOCYANATE *v.* Ethyl sulphocyanide.

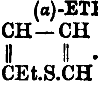
DI-ETHYL-THIONINE



$$N\begin{cases}C_6H_3—NHEt\\ \quad >S\\ C_6H_3—NEt\end{cases}$$

Obtained by the action of Fe$_2$Cl$_6$ upon a dilute solution of ethyl-*p*-phenylene diamine in presence of H$_2$S and HCl. In its properties and reactions it closely resembles the di-methyl-thionine (*q. v.*) (Bernthsen a. Goske, *B.* 20, 933).

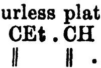
(*α*)-ETHYL-THIOPHENE C$_6$H$_8$S *i.e.*



$$\begin{matrix}CH—CH\\ \| \quad \|\\ CEt.S.CH\end{matrix}$$

. (133° cor.). S.G. ^{24} ·990. Formed by the action of sodium upon a mixture of (*β*)-bromo-thiophene and EtBr (Schleicher, *B.* 18, 3015; 19, 671); or upon EtI or EtBr and (*β*)-iodo-thiophene (Meyer a. Kreis, *B.* 17, 1560; Egli, *B.* 18, 544). Colourless oil. Gives Laubenheimer's reaction. By alkaline KMnO$_4$ it is oxidised to thienyl methyl ketone, thiophene-(*α*)-carboxylic acid [127°], and thienyl-(*α*)-glyoxylic acid. Gives a tri-bromo- derivative C$_4$SEtBr$_3$: [108°]; colourless plates.

(*β*)-Ethyl-thiophene



$$\begin{matrix}CEt.CH\\ \| \quad \|\\ CH.S.CH\end{matrix}$$

. Obtained by heating ethyl-succinic acid with P$_2$S$_5$ (Damsky, *B.* 19, 3284). Oil. KMnO$_4$ gives thiophene (*β*)-carboxylic acid [136°].

Di-ethyl-thiophene C$_4$SH$_2$Et$_2$. (181° cor.). S.G. $\frac{14}{14}$ ·962. From iodo-ethyl-thiophene, EtI, and sodium (Muhlert, *B.* 19, 633).

References. — Bromo-, Chloro-, Iodo-, and Nitro-ethyl-thiophene.

(*α*)-ETHYL-THIOPHENE CARBOXYLIC ACID C$_4$SH$_2$Et.CO$_2$H. *Ethyl-thiophenic acid.* [71°]. Obtained by the action of sodium amalgam upon a mixture of iodo-(*α*)-thiophene and chloro-formic ether, and saponification of the product. Glistening colourless crystals. V. sol. alcohol, ether, and hot water, sl. sol. cold water. By alkaline KMnO$_4$ it is oxidised to thiophene di-carboxylic acid.

Salts.—AgA′: curdy pp., sol. hot water.—CaA′$_2$ 2½aq: colourless silky needles (Schleicher, *B.* 18, 3018).

ETHYL THIOPHOSPHATES.

Mono-ethyl thiophosphate $(EtO)PS(OH)_2$. *Ethyl-thiophosphoric acid.* Oil formed by the action of alcohol on $PSCl_3$. The K and Na salts are formed by treating $PSCl_3$ with alcoholic KOH or NaOH. They are v. sol. water and alcohol. The salts of Ba, Sr, and Ca are crystallisable.—BaA″ (Cloez, *C. R.* 24, 388; Chevrier, *Z.* 1869, 418).

Di-ethyl-thiophosphate $(EtO)_2PS(OH)$. *Di-ethyl-thiophosphoric acid.* Formed, together with $Et_3PS_2O_2$, by the action of P_2S_5 on alcohol (Carius, *A.* 112, 190). Viscid oil, having an acid and bitter taste. It may be boiled in aqueous or alcoholic solution without decomposition, but when heated *per se* it gives off mercaptan and leaves phosphoric acid. It forms very stable salts, those of the alkalis, alkaline earths, and of lead being v. sol. water, sol. absolute alcohol and ether. The silver salt is v. sl. sol. water, but v. sol. alcohol and ether.

Tri-ethyl thiophosphate $(EtO)_3PS$. Formed by the action of alcohol on $PSCl_3$ or $PSBr_3$; and of $PSCl_3$ on NaOEt (Carius, *A.* 119, 291; Chevrier, *Z.* 1869, 413; Michaelis, *B.* 5, 4). Oil, smelling like turpentine, volatile with steam. Conc. H_2SO_4 appears to form $EtPSO_2$ and $Et_4P_2S_2O_5$.

Di-ethyl di-thiophosphate $Et_2HPO_2S_2$. Formed, together with Et_2S, by heating $Et_3PO_2S_2$ with mercaptan in a sealed tube (Carius). The K salt is formed by the action of alcoholic KSEt on $Et_3PO_2S_2$. Colourless amorphous mass.

Tri-ethyl di-thio-phosphate $Et_3PO_2S_2$. Formed, as above, by treating alcohol with P_2S_5. Colourless oil, with aromatic and somewhat alliaceous odour. Volatile with steam.

Di-ethyl tetra-thio-phosphate Et_2HPS_4. The K salt is formed by the action of alcoholic KSH on Et_3PS_4. Et_2HPS_4 crystallises in prisms (Carius, *J.* 1861, 583).

Tri-ethyl tetra-thio-phosphate Et_3PS_4. Produced by the action of P_2S_5 on mercaptan, or, better, on mercury mercaptide (Carius, *A.* 112, 199). Light yellow oil. KOH forms, apparently, KEt_2POS_3.

Tetra-ethyl di-thio-pyrophosphate $Et_4P_2S_2O_5$. Appears to be produced by treating Et_3PSO_3 with conc. H_2SO_4 (Carius, *Z.* 1861, 305). Liquid, m. sol. water. Alcoholic KOH gives $Et_3KP_2S_2O_5$.

Tetra-ethyl tri-thio-pyrophosphate $Et_4P_2S_3O_4$. From $P_2S_3Br_4$ and alcohol (Michaelis, *B.* 5, 8).

Tetra-ethyl penta-thio-pyrophosphate $Et_4P_2S_5O_2$. [71°] (Carius, *J.* 1861, 586).

ETHYL THIOSINAMINE *v.* ETHYL-ALLYL-THIO-UREA.

MONO-ETHYL THIOSULPHATE $EtS.SO_2.OH$. *Ethyl-thiosulphuric acid.*

Formation.—1. By treating Et_2S with an equal volume of conc. H_2SO_4 (R. H. Smith, *C. J.* 22, 302).—2. By heating EtBr (1 mol.) with $Na_2S_2O_3$ (1 mol.) with an inverted condenser (Bunte, *B.* 7, 646).—3. By the action of iodine on a mixture of mercaptan and Na_2SO_3 (Spring, *B.* 7, 1162).

Salts.—NaA′: silky six-sided needles (from alcohol). Its aqueous solution is scarcely decomposed at 100°, but on adding a small quantity of HCl it rapidly splits up into mercaptan and $NaHSO_4$. The dry salt is slowly converted at 100° into dithionate and Et_2S_2. Its aqueous solution gives sparingly soluble pps. with $AgNO_3$, $Pb(NO_3)_2$, and $HgCl_2$; the last pp. is quickly converted on heating into EtSHgCl, while sulphuric acid remains in solution. HNO_3 oxidises the sodium salt to sulphuric and ethane sulphonic acids. Sodium forms mercaptan and Na_2SO_3.—$BaA'_2 2aq$: colourless rectangular tables, v. sol. water, sl. sol. alcohol. The copper salt forms small dimetric tables, v. sol. water. The silver salt crystallises in small shining laminæ.

Chloride $EtS.SO_2Cl$. From the Na salt and PCl_5. Split up by heat, giving Et_2S_2 (*cf.* Ramsay, *B.* 8, 764).

ETHYL-THIO-URAMIDO-BENZOIC ACID $NHEt.CS.NH.C_6H_4.CO_2H$. *Phenyl-ethyl-thio-urea m-carboxylic acid.* [195° uncor.]. Formed by boiling *m*-amido-benzoic acid with ethyl-mustard-oil in alcoholic solution (Aschan, *B.* 17, 430). Small transparent prisms.

ETHYL-THIO-UREA $C_3H_8N_2S$ *i.e.* $NH_2.CS.NHEt$. Mol. w. 104. [113°] (Hofmann, *B.* 18, 2788). From ethyl thio-carbimide by direct addition of NH_3 in alcoholic solution (Hofmann, *Z.* 1868, 686; 1870, 157; *B.* 1, 26). Needles (from hot water). Sol. water and alcohol. Its solution in aqueous HCl gives a yellow pp. with $PtCl_4$. In aqueous or alcoholic solution it is easily desulphurised by PbO or HgO, the ultimate product being tri-ethyl-melamine $C_3N_3(NHEt)_3$.

Benzoyl derivative NHBz.CS.NHEt. [134°]. Obtained by treating benzoyl sulphocyanide with ethylamine (Miquel, *A. Ch.* [5] 11, 313). Slender prisms, insol. water, m. sol. boiling alcohol. Split up by boiling with aqueous HCl, giving ethylamine and benzamide. HgO gives NHBz.CO.NHEt.

Di-ethyl-thio-urea $CS(NHEt)_2$. Mol. w. 132. Formed by the addition of ethylamine to ethyl thiocarbimide; also, with evolution of H_2S, by heating ethylamine ethyl-thio-carbamate with alcohol at 115° (Hofmann). Crystals, sol. alcohol, m. sol. water. Its solution in aqueous HCl gives a yellow crystalline pp. with $PtCl_4$. By P_2O_5 or dry HCl it is resolved into ethylamine and ethyl thiocarbimide. It is not decomposed in aqueous or alcoholic solution by PbO, but recently ppd. HgO converts it into $CO(NHEt)_2$ [107°]. HgO in presence of ethylamine forms tri-ethyl-guanidine.

Tri-ethyl-thiourea $NHEt.CS.NEt_2$. [26°]. (205° uncor.). Prepared by the action of ethyl-thiocarbimide on diethylamine (Grodzki, *B.* 14, 2755). Colourless crystals. Sol. alcohol and ether, nearly insol. water. Alkaline reaction. Potash-fusion gives NH_2Et and $NHEt_2$. P_2O_5 gives ethyl thio-carbimide.

Tetra-ethyl-thiourea $CS(NEt_2)_2$. (216° uncor.). S.G. $\underline{15}$ ·9345 (Grodzki, *B.* 14, 2757). Colourless liquid. Sol. alcohol and ether, insol. water. Strong base of alkaline reaction. Very stable. Prepared by ethylation of tri-ethyl-thiourea.

ETHYL TITANATE Et_4TiO_4. By the action of $TiCl_4$ (1 mol.) on alcohol (4 mols.) there is formed $TiCl_2(OEt)_2EtOH$ [105°-110°] whence NaOEt gives $Ti(OEt)_4$ (Demarçay, *C. R.* 80, 51).

Trichloride $EtOTiCl_3$. [78°]. (187° cor.). From $TiCl_4$ and ether (Bedson, *A.* 180, 235).

o-**ETHYL-TOLUENE** C_9H_{12} *i.e.* $C_6H_4(CH_3)(C_2H_5)$ [1:2]. *Methyl-ethyl-benzene*

Mol. w. 120. (158° uncor.). S.G. ^{18} ·8731. Liquid at − 17°. Obtained by the action of sodium upon a mixture of *o*-bromo-toluene and ethyl bromide. By dilute HNO_3 it is oxidised to *o*-toluic acid, and by $KMnO_4$ to terephthalic acid (?) (Claus a. Mann, *B.* 18, 1121).

***m*-Ethyl-toluene** C_6H_4MeEt [1:3]. (159°). S.G. ^{20} ·869. Formed by boiling an ethereal solution of EtBr and *m*-bromo-toluene with sodium for two days (Wroblewsky, *A.* 192, 198). Formed also by distilling abietic acid with zinc-dust (Ciamician, *B.* 11, 270). By oxidation with CrO_3 it yields isophthalic acid. H_2SO_4 forms two sulphonic acids; the Ba salt of one of these BaA'_2 6aq forms large crystals, sl. sol. water; that of the other forms small prisms, v. sol. water

Dihydride? C_9H_{14}. (154°). Occurs in animal oil (Weidel a. Ciamician, *B.* 13, 72). Gives isophthalic acid on oxidation.

Sulphonic acids $C_6H_3MeEtSO_3H$. — BaA'_2 6aq.—BaA'_2 8aq.

***p*-Ethyl-toluene** C_6H_4MeEt [1:4]. (161·9°–162·1°) at 756·3 mm. S.G. $\frac{11\cdot3}{4}$ ·8694 (Schiff); $\frac{20}{4}$ ·864 (A.). V.D. 4·11 (calc. 4·14). S.V. 161·9 (Schiff, *A.* 220, 93). Formed by treating *p*-bromo-toluene with ethyl bromide and sodium (Glinzer a. Fittig, *A.* 136, 303; Jannasch a. Dieckmann, *B.* 7, 1513). Formed also from ethylidene chloride, toluene, and Al_2Cl_6 (Anschütz, *A.* 235, 314). Converted by $K_2Cr_2O_7$ and H_2SO_4 into *p*-toluic and terephthalic acids.

References.—Bromo-, Chloro-, and Nitro-ethyl-toluene.

Di-ethyl-toluene $C_6H_3MeEt_2$ [1:3:5]. (199°). S.G. $\frac{20}{}$ ·879. From acetone, methyl ethyl ketone, and H_2SO_4 (Jacobsen, *B.* 7, 1434). HNO_3 oxidises it to uvitic acid.

Isomeride *v.* Amyl-benzene.

ETHYL-*o*-TOLUIDINE $C_9H_{13}N$ *i.e.* $C_6H_4(CH_3).NHEt$. (214°) (R. a. S.); (206°) (N.). S.G. $\frac{15\cdot5}{15\cdot5}$ ·9534. Prepared by heating *o*-toluidine hydrobromide (or hydroiodide) with 1 mol. (+ 5 p.c. excess) of ethyl alcohol at 150° for 8 hours; the yield is 54 p.c. of the theoretical.

Acetyl derivative $C_6H_4(CH_3).NAcEt$. (255°) (Reinhardt a. Staedel, *B.* 16, 29; Norton, *Am.* 7, 118).

Nitrosamine $C_6H_4Me.NEt.NO$. Oil; volatile with steam.

Ethyl-*p*-toluidine $C_6H_4Me.NHEt$ [1:4]. (217°). S.G. $\frac{15\cdot5}{}$ ·9391. From *p*-toluidine and EtI by heating for 2 days at 100° (Morley a. Abel, *C. J.* 7, 68). Oil. Its sulphate and oxalate are crystalline.—$B'_2H_2PtCl_6$: pale-yellow crystals, sol. water and alcohol, sl. sol. ether; decomposed at 100°.

Di-ethyl-*o*-toluidine $C_6H_4(CH_3).NEt_2$. (208°) at 755 mm.; (210° i. V.) (R.). Formed by heating ethyl-*o*-toluidine with excess of EtI at 100°; the yield being 70 p.c. (Norton, *Am.* 7, 119). Prepared by heating *o*-toluidine hydrobromide (or hydroiodide) with 2 mols. (+ 5 p.c. excess) of ethyl alcohol at 150° for 8 hours; the yield is 90 p.c. of the theoretical (Reinhardt a. Staedel, *B.* 16, 29). Oil. Fuming nitric acid yields $C_6H_2Me(NO_2)_2N(NO_2)Et$ [72°] (Van Romburgh, *R. T. C.* 3, 402).

Salt.—$B'HI$ aq: [73°]; prisms.

Di-ethyl-*p* toluidine $C_6H_4(CH_3).NEt_2$ [1:4]. (228°). S.G. $\frac{15\cdot5}{}$ ·9242. Formed by heating ethyl-*p*-toluidine with EtI (Morley a. Abel). Prepared by heating *p*-toluidine hydrobromide (or hydroiodide) with 2 mols. (+ 5 p.c. excess) of ethyl alcohol at 150° for 8 hours; the yield is 95 p.c. of the theoretical (Reinhardt a. Staedel, *B.* 16, 29). Oil. Nitric acid (S.G. 1·5) yields $C_6H_2Me(NO_2).NEt(NO_2)$ (Van Romburgh, *R. T. C.* 3, 408). Diazo-benzene chloride gives $C_6H_5.N_2.NEt.C_6H_4Me$ [38°]; diazo-*m*-nitro-benzene chloride reacts with formation of [3:1] $C_6H_4(NO_2).N_2.NEtC_6H_4Me$ [55°]; while diazo-*p*-nitro-benzene chloride gives rise to [4:1] $C_6H_4(NO_2).N_2.NEt.C_6H_4Me$ [114°] (Noelting a. Binder, *Bl.* [2] 49, 81).—$B'_2H_2PtCl_6$: rhombohedra (Söffing, *P. B.* 8, 190).—$B'HClHgCl_2$ $\frac{1}{2}$aq: triclinic crystals.—$B'HBr$: monoclinic crystals. —$B'HI$: crystalline.—$B'HNO_3$: monoclinic crystals.

Ethylo-iodide $C_6H_4Me.NEt_3I$. Heavy oil. Decomposed by moist Ag_2O it gives the strongly alkaline $C_6H_4Me.NEt_3OH$, whence $(C_6H_4MeNEt_3Cl)_2PtCl_4$ which crystallises from hot water in slender needles (Morley a. Abel).

ETHYL-DI-TOLYL-AMINE *v.* Di-tolyl-ethyl-amine.

ETHYL-TOLYLENE-DIAMINE *v.* Tolylene-ethyl-diamine.

ETHYL-TOLYL- *v.* Tolyl-ethyl-.

ETHYL-TROPIC ACID *v.* tropic acid under α-Oxy-α-phenyl-propionic acid.

ETHYL-ULTRAMARINE. Prepared by heating in sealed tubes silver ultramarine and ethyl iodide, to the solid residue a further quantity of the iodide is added and the process repeated until all the silver is removed. A grey substance, evolving ethyl sulphide when heated to 100°. With sodium chloride it forms ordinary sodium ultramarine and ethyl chloride (De Forcrand, *A. Ch.* [5] 17, 564; *C. R.* 88, 30).

DI-ETHYL-UMBELLIC ACID *v.* Umbellic acid.

ETHYL-URAMIDO-BENZOIC ACID $C_{10}H_{12}N_2O_3$ *i.e.* $NHEt.CO.NH.C_6H_4.CO_2Et$. From cyanic ether and *m*-amido-benzoic acid in alcoholic solution (Griess, *J. pr.* [2] 5, 454). Slender needles. V. sl. sol. boiling water, v. e. sol. boiling alcohol. Acid in reaction. — BaA'_2 3aq: minute needles.—AgA': laminæ.

Reference. — Amido-ethyl-uramido-benzoic acid.

ETHYL-UREA $C_3H_8N_2O$ *i.e.* $CO(NH_2)(NHEt)$. Mol. w. 88. [92°]. S.G. $\frac{18}{}$ 1·213.

Formation.—1. By the union of cyanic ether with ammonia (Wurtz, *C. R.* 32, 414).—2. By the union of ethylamine with cyanic acid (Leuckart, *J. pr.* [2] 21, 10).

Properties.—Large deliquescent prisms (from alcohol); excessively sol. water, alcohol, chloroform, CS_2, and boiling benzene. Insol. ether. At 200° it decomposes with evolution of NH_3 and a little NH_2Et, leaving a residue containing di-ethyl cyanurate (Wurtz, *Rép. Chim. Pure*, 1862, 199).

Reactions.—1. *Nitrous acid* forms alcohol, nitrogen, and CO_2. NaOH acts in like manner.—2. A boiling aqueous solution dissolves *mercuric oxide*, and on cooling deposits crystals containing 53·5 p.c. of mercury (L.).—3. Evaporation with $AgNO_3$ forms silver cyanate.—4. *Aniline* at 150°

forms di-phenyl-urea, NH_2Et, and NH_3 (L.).—5. Alcoholic KOH at 100° gives potassium cyanate and ethylamine (Haller, *Bl.* [2] 45, 705).

Salts.—$B'HNO_3$: rosettes of thick prisms Melts below 60° and then decomposes. V. sol. cold water and alcohol.—B'HCl. Got by passing HCl over the base at 100°. At 160° it gives off ethylamine.—$B'_2H_2C_2O_4$: [c. 60°]; rectangular plates, v. sol. water and alcohol.

Acetyl derivative CON_2H_2EtAc. [c. 120°]. From ethyl-urea and ClAc. Stout prisms (from ether). Readily sol. water, alcohol, and ether. Sublimes in long needles. Boiled with KOH it forms potassic carbonate and acetate, NH_3, and $NEtH_2$.

Propionyl derivative CO(NHEt)(NH.COEt). [100°]. Fine needles. Sol. water. alcohol, and ether. Formed from propionamide, Br, and NaOHAq (Hofmann, *B.* 15, 754).

s-Benzoyl derivative CO(NHEt)(NHBz). [168°] (L.); [192°] (M.). From ethyl-urea and BzCl at 130° (Leuckart, *J. pr.* [2] 21, 33). Also from the benzoyl derivative of ethyl-thio-urea by treatment with ppd. HgO (Miquel, *A. Ch.* [5] 11, 318). Needles (from water). V. sol. alcohol, ether, and hot water.

u-Benzoyl derivative NH_2.CO.NEtBz. From EtS.CO.NEtBz and cold alcoholic NH_3 (Lössner, *J. pr.* [2] 10, 251). Rhombohedra (from dilute alcohol). V. e. sol. absolute alcohol, m. sol. ether, v. sl. sol. water.

s-Di-ethyl-urea $CO(NHEt)_2$. Mol. w. 116. [106°] (L. a. H.); [109°-112·5°] (W.). (263° cor.).

Formation.—1. From ethylamine and cyanic ether. Hence formed also by the action of water on cyanic ether (Wurtz, *C. R.* 32, 414).—2. Formed, together with cyanic ether, by the distillation of tri-ethyl-biuret (Limpricht a. Habich, *A.* 109, 105).

Properties.—Silky flexible needles (from alcohol). V. sol. water, alcohol, and ether.

Reactions.—1. Gives off ethylamine when boiled with *potash.*—2. Heated in sealed tubes at 100° with alcoholic KOH it gives potassium cyanate and diethylamine (Haller, *Bl.* [2] 45, 706).

Salts.—$B'HNO_3$: very acid deliquescent prisms.

Nitrosamine NHEt.CO.NEt.NO. [5°]. Formed by heating di-ethyl-urea with nitrous acid (Von Zotta, *A.* 179, 102; E. Fischer, *A.* 199, 284; *B.* 9, 111). Tables; sl. sol. water. Decomposed by heat, even below 100°, into nitrogen, ethylene, and cyanic ether. Gives Liebermann's reaction with phenol and H_2SO_4. Reduced by zinc and acetic acid to di-ethyl-semicarbazide.

u-Di-ethyl-urea $CO(NH_2)(NEt_2)$. [70°]. From diethylamine and cyanic acid (Volhard, *A.* 119, 360; A. P. N. Franchimont, *R. T. C.* 2, 122). Crystals, very sweet taste. V. sol. ether and alcohol. Sol. HNO_3 with absorption of heat, but afterwards a strong reaction sets in, and heat is given out; CO_2 and a little N_2O being evolved, the liquid then yielding crystals of nitro-di-methyl-amine (di-methyl-nitro-amide) $(CH_3)_2$:N.NO_2 [57°].

Tri-ethyl-urea $CO(NHEt)(NEt_2)$. [63°]. (c. 235°). From cyanic ether and diethylamine; formed also by treating triethylamine with vapour of cyanic acid (Wurtz; Hofmann, *Pr.* 11, 273). Soft crystals, sol. water, alcohol, and ether. It does not appear to combine with acids. Alkalis convert it into ethylamine, diethylamine, and CO_2.

Tetra-ethyl-urea $CO(NEt_2)_2$. (205°) (M.); (210°-215°) (W.).

Formation.—1. By passing $COCl_2$ into a solution of diethylamine in ligroïn (Michler, *B.* 8, 1664).—2. From Cl.CO.NEt_2 and diethylamine (Wallach, *A.* 214, 275).

Properties.—Oil. Dissolves in acids, but is reppd. by alkalis.

ETHYL-URETHANE *v.* ETHYL THIOCARBAMIC ACID.

ETHYL-VINYL *v.* BUTINENE.

ETHYL-VINYL OXIDE *v.* VINYL ETHYL OXIDE.

DI-ETHYL-XANTHAMIDE *v.* ETHYL-DI-THIO-CARBAMIC ACID.

ETHYL-o-XYLENE $C_6H_3Me_2Et$ [1:2:4]. *Di-methyl-ethyl-benzene.* (189°). From camphor and $ZnCl_2$ or iodine (Armstrong a. Miller, *C. J.* 45, 148; *B.* 16, 2258). Also from bromo-*o*-xylene, EtBr, and sodium (Jacobsen, *B.* 19, 2516). Gives on oxidation $C_6H_3Me_2CO_2H$.

Sulphonic acid $C_6H_2Me_2EtSO_3H$. Tables. —$BaA'_2$4aq.

Amide $C_6H_2Me_2EtSO_2NH_2$. [126°]. Needles or prisms (from alcohol).

Ethyl-m-xylene $C_6H_3Me_2Et$ [1:3:5]. (187°). S.G. $\frac{20}{4}$ ·869. From ethylidene chloride, Al_2Cl_6, and xylene (Anschütz, *A.* 235, 323). Formed also by treating a mixture of acetone and methyl ethyl ketone with H_2SO_4 (Jacobsen, *B.* 7, 1432); and by treating (1,3,5)-bromo-xylene with EtBr and sodium (Wroblewsky, *A.* 192, 217). Bromine forms a tribromo- derivative [91°]. On oxidation it gives uvitic acid $C_6H_3Me(CO_2H)_2$ [290°].

Ethyl-m-xylene $C_6H_3Me_2Et$ [1:3:4]. (184°). S.G. ^{20} ·878. From bromo-*m*-xylene, EtBr, and sodium (Fittig a. Ernst, *A.* 139, 184; *Z.* [2] 1, 572). Liquid. Gives a tri-nitro- derivative [119°].

Sulphonic acid $C_6H_2Me_2Et.SO_3H$. Crystalline mass (J.).—BaA'_2 2aq: trimetric laminæ, m. sol. cold water.—NaA' 2aq: minute flat prisms, v. e. sol. cold water.

Amide $C_6H_2Me_2Et.SO_2NH_2$. [148°]. Needles or prisms (from alcohol).

Ethyl-p-xylene $C_6H_3Me_2Et$ [1:4:3]. (185°). From (3,1,4)-bromo-*p*-xylene, EtBr, and sodium (Jacobsen, *B.* 19, 2516). It gives a tri-nitro-derivative [120°].

Sulphonic acid $C_6H_2Me_2Et.SO_3H$. Large trimetric plates (from dilute H_2SO_4).—NaA' aq: tables; m. sol. cold water.—BaA'_2: six-sided plates, m. sol. boiling water.

Amide $C_6H_2Me_2EtSO_2NH_2$. [117°]. Pearly plates (from very dilute alcohol); m. sol. cold alcohol.

Reference.—TRI-BROMO-ETHYL-XYLENE.

ETHYL-XYLYL *v.* XYLYL-ETHYL.

ETTIDINE. A name given by Greville Williams (*Laboratory,* 109) to a base $C_{18}H_{19}N$ obtained by distilling quinoline with KOH.

EUCALYN $C_6H_{12}O_6$ aq. $[\alpha]$ = about 50°. A sweet, syrupy substance produced, together with glucose, by boiling melitose $C_{12}H_{22}O_{11}$ (the sugar of the eucalyptus) with dilute sulphuric acid, and obtained, together with alcohol, by fermenting melitose with yeast (Berthelot, *A. Ch.* [3] 46, 72). Dextro-rotatory, and non-fermentable. It becomes coloured at 100°, and at 200° it forms a black insoluble substance. Dilute H_2SO_4 does not affect it. Boiling baryta-water colours it strongly. It reduces Fehling's solution.

EUCALYPTENE. This name was applied by Cloez (*A.* 154, 372) to a hydrocarbon $C_{10}H_{16}$? (165°); S.G. ^{12} ·836; V.D. 5·3, obtained by distilling eucalyptol with P_2O_5. The same name was applied by Faust a. Homeyer (*B.* 7, 63, 1429), and by Oppenheim a. Pfaff, (*B.* 7, 625) to a terpene (172°–175°), V.D. 68·4, said to occur in oil of eucalyptus.

EUCALYPTOL $C_{10}H_{18}O$. [1°]. (172°) (V.); (176° i.V.) (J.). S.G. ^{16} ·923 (J.); ^{0} ·940. Occurs in the oil of *Eucalyptus Globulus* and is isolated from the fraction 170°–180° by conversion into the hydrochloride (Jahns, *B.* 17, 2941). Optically inactive. Probably identical with cineol. Camphor-like smell. Colourless liquid. Dry HCl forms the compound $(C_{10}H_{18}O)_2HCl$ (Voiry, *C. R.* 106, 1419). $KMnO_4$ oxidises it to cineolic acid $C_{10}H_{16}O_5$ [196°] (Wallach, *A.* 246, 265).

EUCALYPTUS MANNA *v.* MELITOSE.

EUCALYPTUS OIL. The essential oil of *Eucalyptus Globulus* is a pale-yellow, slightly dextrorotatory liquid. S.G. ·932. At −50° it solidifies, and the crystals thus formed melt at −10°. On distillation the first fractions contain water, formic and acetic acids, and butyric and valeric anhydrides. At 159° there passes over a terpene S.G. ·88;, $[\alpha]_D = +40°$, which forms a hydrochloride $C_{10}H_{16}HCl$ [127°]; $[\alpha]_D = 27\frac{1}{2}°$. The fraction 170°–175° contains eucalyptol which constitutes two-thirds of the oil of eucalyptus (Voiry, *C. R.* 106, 1419; *cf.* Cloez, *A.* 154, 372). According to Faust a. Homeyer (*B.* 7, 63, 1429) oil of eucalyptus contains two terpenes (151°) and (c. 174°), together with cymene and a camphor-like body $C_{10}H_{16}O$. Oppenheim a. Pfaff found in Australian eucalyptus oil a terpene (173°) whence iodine produces cymene. Wallach found in the Australian oil (from *E. amygdalina*) cineol and a lævorotatory phellandrene (165°–180°). S.G. ^{18} ·855 (Wallach, *A.* 246, 265).

EUCHROIC ACID *v.* *Di-imide* of MELLITIC ACID.

EUCHLORINE. This name was given by Davy to a gas obtained by the reaction between HClAq and $KClO_3$; it has been proved to be a mixture of ClO_2 and Cl (*cf.* p. 12). M. M. P. M.

EUDIOMETER. A graduated glass vessel used in analysis of gases, and in titrimetric analysis (*v.* vol. i. pp. 237 and 248). M. M. P. M.

EUGENOL $C_{10}H_{12}O_2$ *i.e.* [1:3:4] $C_6H_3(OH)(OMe).CH_2.CH:CH_2$. Mol. w. 164. V.D. 6·4 (calc. 5·7). (242°) (S.); (251°) (Williams); (252°) (Gladstone); (252° cor.) (Church). S.G. ^{4} 1·068 (W.); ^{20} 1·066 (G.); ^{15} 1·066 (Church, *C. J.* 28, 113); ^{0} 1·079 (Wassermann); $^{18·5}$ 1·063 (Wa.); ^{14} 1·070 (Tiemann a. Kraaz, *B.* 15, 2066). μ_D 1·540. μ_γ 1·554.

Occurrence.—In oil of cloves; in oil of bay (*Laurus nobilis*); in the oil of cinnamon leaves; in oil of pimento; in oil of *Canella alba*; and in oil of *Ilicium religiosum* (Bonastre, *A. Ch.* [1827] 35, 274; Dumas, *A. Ch.* 53, 164; *A.* 9, 65; 27, 151; Ettling, *A.* 9, 68; Böckmann, *A.* 27, 155; Greville Williams, *Chem. Gaz.* 1858, 170; Cahours, *A. Ch.* [3] 52, 201; Stenhouse, *A.* 95, 103; Wöhler, *A.* 47, 236; Baeyer, *A.* 114, 163; Gladstone, *C. J.* 17, 6; Oeser, *A.* 131, 277; Eykman, *R. T. C.* 4, 33; Erlenmeyer, *Z.* 1866, 430; Wassermann, *A.* 179, 366).

Formation.—By reducing coniferin in weak alkaline solution with sodium-amalgam; coniferyl alcohol being an intermediate product (Tiemann, *B.* 9, 418; Chiozza, *C. C.* 1888, 443).

Preparation.—Oil of cloves, obtained by distilling cloves with water, contains eugenol and a terpene. Aqueous KOH dissolves the eugenol, and, on again distilling, only the terpene passes over. On acidifying the residue the eugenol is liberated.

Properties.—Colourless oil, with spicy odour. Reddens litmus. Quickly resinifies when exposed to air. V. sl. sol. water, v. sol. alcohol, ether, and HOAc. Has a burning taste. Does not reduce Fehling's solution. Reduces ammoniacal silver nitrate. $FeCl_3$ colours its alcoholic solution blue.

Reactions.—1. Distillation over BaO gives an oil (142°) (Calvi, *A.* 99, 242; Church, *P. M.* [4] 9, 256).—2. Distilled with HI it forms MeI and a resinous mass having nearly the composition $C_9H_{10}O_2$ (Erlenmeyer, *Z.* [2] 2, 430).—3. *Potash-fusion* gives acetic and protocatechuic acids (Hlasiwetz a. Grabowski, *A.* 139, 95).—4. P_2O_5 forms a resin, intermediate in composition between $C_{10}H_{12}O_2$ and $C_{10}H_{12}O_3$, which on distillation yields a phenol which is coloured green by $FeCl_3$ (Hlasiwetz a. Barth, *Z.* [2] 2, 83).—5. PCl_5 forms HCl, MeCl, an oily anhydride (?) $(C_{10}H_{11}O)_2O$, and an amorphous yellow compound $C_{10}H_{13}PO_4$; insol. ether (Oeser, *A.* 131, 277).—6. *Bromine* forms di-bromo-eugenol di-bromide (*q.v.*). Acetyl-di-bromo-eugenol crystallises from ether in hexagonal prisms [66°] (Boyen, *B.* 21, 1393). The acetyl and benzoyl derivatives of di-bromo-eugenol dibromide melt at [91°] and [113°] respectively.—7. $KMnO_4$ oxidises it to vanillin, the methyl derivative of protocatechuic aldehyde.—8. Vapour of *cyanic acid* passed into eugenol forms the crystalline allophanate $C_6H_3(OMe)(C_3H_5).O.CO.NH.CO.NH_2$ (Baeyer, *A.* 114, 163).—9. *Phenyl cyanate* at 100° forms $C_6H_3(C_3H_5)(OMe).O.CO.NHPh$ [96°] (Snape, *B.* 18, 2432; *C. J.* 47, 777).—10. *Chloro-acetic acid* acting on sodium-eugenol forms the acid $C_6H_3(OMe)(C_3H_5).O.CH_2.CO_2H$ [81°], which crystallises from hot water in long needles, sol. aqueous Na_2CO_3. Its sodium salt NaA′1½ aq is v. sol. cold water (Saarbach, *J. pr.* [2] 21, 151).—11. *Acetochlorhydrose* converts potassium eugenol into the glucoside $C_6H_3(O.C_6H_{11}O_5)(OMe)C_3H_5$ [132°]. This crystallises in needles, sol. hot alcohol, hot benzene, and hot water (Michael, *Am.* 6, 340).

Metallic derivatives $NaC_{10}H_{11}O_2$.—$HK(C_{10}H_{11}O_2)_2$ aq.—$Ba(C_{10}H_{11}O_2)_2$: laminæ, sl. sol. cold water.

Acetyl derivative $C_6H_3(OAc)(OMe).C_3H_5$. [31°]. (270°). Prepared by boiling eugenol with Ac_2O for three hours. Crystals; v. sol. alcohol and ether, insol. water and cold dilute alkalis.

Conc. H_2SO_4 dissolves it with deep-red colour. $KMnO_4$ oxidises it to acetyl vanillic acid $C_{10}H_{10}O_5$ and its homologue $C_{11}H_{12}O_5$ (Tiemann a. Nagai, *B.* 10, 202).

Carbonyl derivative $(C_6H_3(OMe)(C_3H_5).O)_2CO$. [93°]. From sodium eugenol and $COCl_2$ (Löwenberg, *C. C.* 1886, 390; *C. J.* 50, 789).

Benzoyl derivative $C_6H_3(OBz)(OMe)(C_3H_5)$: [70°]; monosymmetrical crystals; sl. sol. cold alcohol, insol. water (Tiemann a. Kraaz, *B.* 15, 2067).

p-Methoxy-benzoyl derivative $C_6H_3(O.CO.C_6H_4OMe)(OMe)C_3H_5$. From eugenol and anisyl chloride (Cahours, *A. Ch.* [3] 52, 189). Crystalline.

Methyl ether $C_{11}H_{14}O_2$ *i.e.* $C_6H_3(OMe)_2.C_3H_5$. (245°). Obtained from $C_6H_3(ONa)(OMe).C_3H_5$ and MeI (Graebe a. Borgmann, *A.* 158, 282; Matsmoto, *B.* 11, 123). Oxidised by $K_2Cr_2O_7$ in HOAc to $C_6H_3(OMe)_2CO_2H$. $KMnO_4$ gives an acid $C_{12}H_{12}O_5$ [163°]. Bromine gives $C_6H_2Br(OMe)_2.CH_2.CHBr.CH_2Br$ [78°], which, in alcoholic solution, is converted by zinc-dust into liquid $C_6H_2Br(OMe)_2.C_3H_5$. A mercury salt $Hg(C_{11}H_{13}O_2)_2$ [140°] is formed as a by-product in the formation of $C_6H_2(OMe)_2(C_3H_5)CO_2H$ by treating $C_6H_2Br(OMe)_2CO_2H$ with $ClCO_2Et$ and sodium-amalgam (Wassermann, *C. R.* 88, 1206).

Ethyl ether $C_{12}H_{16}O_2$ *i.e.* $C_6H_3(OEt)(OMe).C_3H_5$ (254°). S.G. ^{0} 1·026; $\underline{^{18·5}}$ 1·012. From eugenol (50 pts.), KOH (17 pts.), water (40 pts.), and EtBr (33 pts.) by heating at 100° with inverted condenser (Wassermann, *A.* 179, 366). Oil. Gives on oxidation $C_6H_3(OEt)(OMe).CO_2H$. When distilled it partly polymerises, forming crystalline laminæ (from alcohol) [125°]. Bromine forms $C_{12}H_{15}Br_3O_2$ [80°], whence zinc and alcohol remove bromine, leaving $C_{12}H_{15}BrO_2$ [48°], a product which is not acted on by AgOAc.

Propyl-ether $C_6H_3(OPr)(OMe)C_3H_5$. (264°). S.G. $\underline{^{19}}$ 1·002. From eugenol (100 pts.), propyl iodide (100 pts.), and KOH (35 pts.) dissolved in alcohol. Liquid, smelling like cloves. Hot dilute $KMnO_4$ gives $C_6H_3(OPr)(OMe).CO_2H$.

Isopropyl-ether $C_6H_3(OPr)(OMe).C_3H_5$. (253°). S.G. $\underline{^{17}}$ ·999.

Isobutyl ether $C_6H_3(OCH_2Pr)(OMe).C_3H_5$. (273°). S.G. $\underline{^{15}}$ ·985. Oxidised by $KMnO_4$ to $C_6H_3(OCH_2Pr)(OMe).CO_2H$.

Isoamyl ether $C_6H_3(OC_5H_{11})(OMe).C_3H_5$. (284°). S.G. $\underline{^{16}}$ ·976. $KMnO_4$ at 80° forms $C_6H_3(OC_5H_{11})(OMe).CO_2H$.

Hexyl ether $C_6H_3(OC_6H_{13})(OMe).C_3H_5$. (c. 298°).

Allyl ether $C_6H_3(OC_3H_5)(OMe).C_3H_5$. (c. 269°). S.G. $\underline{^{15}}$ 1·018. From allyl iodide and potassium eugenol. A polymeride (284°–290°) is formed at the same time.

Benzyl ether $C_6H_3(OC_7H_7)(OMe).C_3H_5$. Partially decomposed on distillation.

Ethylene ether $C_2H_4(O.C_6H_3(OMe).C_3H_5)_2$. [89°]. Formed by heating eugenol, ethylene bromide, and alcoholic KOH in a sealed tube (Cahours, *C. R.* 84, 157, 1195). Micaceous plates; insol. water and cold alcohol, sol. hot alcohol and ether. $KMnO_4$ oxidises it to

$C_2H_4(O.C_6H_3(OMe).CO_2H)_2$.

Trimethylene ether $C_3H_6(O.C_6H_3(OMe).C_3H_5)_2$. [83°]. From $CH_2Br.CH_2.CH_2Br$, potassium-eugenol, and a little alcohol at 100°. Satiny crystals (from ether) or prisms (from alcohol). $KMnO_4$ gives $C_3H_6(O.C_6H_3(OMe).CO_2H)_2$.

Propylene ether $C_3H_6(O.C_6H_3(OMe).C_3H_5)_2$. [c. 58°]. Prepared as above, using propylene bromide $CH_3.CHBr.CH_2Br$ (Cahours). Needles (from ether).

References. — Bromo-eugenol and Nitro-eugenol.

Iso-eugenol $C_6H_3(OH)(OMe)(CH:CH.CH_3)$ [4:3:1]. (c. 260°). V.D. (H = 1) 82·66 (obs.). S.G. $\underline{^{16}}$ 1·08. Formed by splitting off CO_2 from homoferulic acid by heating to c. 250° or 300° (Tiemann a. Kraaz, *B.* 15, 2064). Oil. Dissolves in H_2SO_4 to a red solution. Fe_2Cl_6 produces a light-green colouration, turned violet by NH_3.

Benzoyl derivative $C_6H_3(OBz)(OMe)(C_3H_5)$. (160°).

EUGETIC ACID $C_{11}H_{12}O_4$ *i.e.* $C_6H_2(OMe)(OH)(C_3H_5)(CO_2H)$ [3:4:1:5]. [124°]. Formed by dissolving sodium in eugenol and passing CO_2 over the resulting sodium eugenol (Scheuch, *A.* 125, 14). Long colourless prisms (from hot water); sl. sol. cold water, v. sol. alcohol and ether. Its aqueous solution is coloured blue by $FeCl_3$. The acid is resolved by heat into CO_2 and eugenol.

Methyl derivative $C_6H_2(OMe)_2(C_3H_5).CO_2H$. [180°]. Formed by saponifying its ether, which is produced by treating the methyl derivative of bromo-eugenol with $ClCO_2Et$ and sodium-amalgam (Wassermann, *C. R.* 88, 1206). Flat yellow needles; sl. sol. water, v. sol. alcohol and ether. Gives on oxidation by $KMnO_4$ an acid [163°].

EULYSIN $C_{24}H_{36}O_3$. A substance which may be extracted along with cerisin and decacrylic acid from cork by boiling with alcohol. It is v. sol. alcohol, but insol. water (Siewert, *Z.* 1868, 383).

EULYTE $C_6H_6N_4O_7$. [99·5° cor.]. S. ·01 at 10°. Formed, together with dyslyte, by treating citraconic acid with strong nitric acid (Baup, *A.* 81, 96; Bassett, *C. J.* 25, 98). Eulyte is the more soluble, it crystallises from chloroform in large dimetric crystals. Heated with alcoholic KOH it forms KNO_2 and a brown resin soluble in alkalis. Tin and HCl give NH_3 and a volatile base smelling like picoline.

EUONYMIN. A bitter resin obtained from the oil of the spindle-tree, *Euonymus europæus* (Riederer, *Buch. Rep.* 14, 1; Grundner, *Buch. Rep.* 97, 315). Insol. water, sol. alcohol and ether, separating from the latter in warty crystals.

The same name is given by Romm (*C. C.* 1885, 442; *C. J.* 50, 72) to a glucoside which may be extracted by dilute alcohol (70 p.c.) from the rinds of *Euonymus atropurpureus*. It may be crystallised from ether.

EUPHORBIUM. A resin consisting of the concrete juice of several species of *Euphorbia* growing in hot climates. Cold alcohol extracts, according to Johnston (*J. pr.* 26, 145), a brownish-red resin $C_{20}H_{30}O_3$, insol. alkalis, but dissolving with red colour in conc. H_2SO_4. Boiling alcohol extracts from the residue another resin $C_{20}H_{32}O_2$, which separates in indistinct crystals

(H. Rose, *P.* 33, 33; 53, 365; Flückiger, *J.* 1868, 809). According to Henke (*Ar. Ph.* [3] 24, 729) euphorbium contains, besides euphorbone, two resins, one soluble in ether, the other not.

EUPHORBONE $C_{20}H_{36}O$. [68°]. $[\alpha]_D = 15{\cdot}9°$. S. ·01 (hot). Extracted from euphorbium by light petroleum at 70° and crystallised from alcohol-ether (Henke, *Ar. Ph.* [3] 24, 729; *cf.* Flückiger, *Z.* [2] 4, 221). Brilliant crystals, persistent in the air, tasteless, and neutral in solution. V. sol. light petroleum, chloroform, ether, alcohol, benzene, and acetone. Not affected by dilute acids, alkalis, or Ac_2O. Heating with P_2O_5 gives heptane, octane, and xylene. According to Hesse (*A.* 192, 193) euphorbone is $C_{15}H_{24}O$ [114°], $[\alpha]_D = 18{\cdot}8°$ at 15° (in chloroform); or 11·7° (in ether).

EUPITTONIC ACID $C_{25}H_{26}O_9$. [about 200°]. Occurs amongst the products of oxidation of wood-tar oil (Liebermann, *B.* 9, 334; Grätzel, *B.* 11, 2085). Prepared by heating the dimethyl ether of pyrogallol with C_2Cl_6 and alcoholic KOH (Hofmann, *B.* 11, 1455). Formed also by heating a mixture of the di-methyl ethers of pyrogallol ($C_6H_3(OMe)_2OH$) and of methyl-pyrogallol ($Me.C_6H_2(OMe)_2OH$) with NaOH at 210°, hydrogen being liberated (Hofmann, *B.* 12, 1377). Long fine orange needles. Difficultly soluble in boiling alcohol, easily in acetic acid. Alkaline solutions are deep blue. By an excess of alkali blue salts are precipitated. HCl at 100° gives pyrogallol and MeCl. Alcoholic NH_3 at 170° gives crystalline $C_{25}H_{31}N_3O_7$. Water (2 pts.) at 265° gives $C_6H_3(OMe)_2OH$ and a crystalline body.

Salts. — $Na_2C_{25}H_{24}O_9\,x$aq: prisms. — $BaC_{25}H_{24}O_9\,x$aq: needles.

Di-acetyl derivative $C_{25}H_{24}O_7(OAc)_2$: [265°]; yellow needles.

Di-benzoyl derivative $C_{25}H_{24}O_7(OBz)_2$: [232°]; small yellow needles. Insol. alcohol, sol. chloroform.

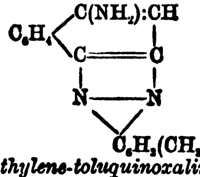
Methyl ether $C_{25}H_{24}O_7(OMe)_2$: [242°]; yellow needles.

Ethyl ether $C_{25}H_{24}O_7(OEt)_2$: [242°]; yellow needles.

Periodide $C_{25}H_{26}O_9I_4$: brown glistening prisms (Hofmann, *B.* 12, 2216).

EURHODINES is the name given by Witt to a class of red colouring matters which have the constitution of amido-quinoxalines. These bodies are produced: (1) By the action of a tri-amine (amido-*o*-diamine) upon a quinone or di-ketone. (2) By heating an *o*-amido-azo- compound with (α)-naphthylamine hydrochloride. Quite recently (*B.* 21, 2418) Witt has proposed to extend the meaning of the term eurhodine so as to include all poly-amido-derivatives of azines.

The eurhodine from *o*-amido-azo-toluene and (α)-naphthylamine has the constitution:



(*amido-naphthylene-toluquinoxalin* or *amido-tolu-naphthazine*). This compound crystallises from aniline or phenol in dark orange needles, almost insol. alcohol and ether. It may be sublimed. Its hydrochloride $C_{17}H_{13}N_3HCl$aq forms garnet-coloured needles. Conc. H_2SO_4 dissolves it with intense red colour turned green and then scarlet on gradual dilution. It dyes silk scarlet in an acid bath. The tartrate dyes cotton mordanted with Turkey-red oil a colour similar to Turkey-red (Witt, *C. J.* 49, 391; *B.* 18, 1119; 19, 914); ethyl nitrite decomposes the eurhodine in alcoholic solution, one product being lemon-yellow needles $C_{19}H_{16}N_2O$ *i.e.* $C_{17}H_{11}EtN_2O$ [175°].

The eurhodine from (β)-naphthylamine is formed on adding quinone dichlorimide to (β)-naphthylamine dissolved in alcohol the solution becoming red and, on adding water, a eurhodine $C_{10}H_6.N_2.C_6H_3NH_2$ (or, more probably, $C_{10}H_5(NH_2).N_2.C_6H_4$) separates. This crystallises from benzene in dark yellow needles, m. sol. alcohol and benzene, v. sol. aniline. Its alcoholic solution is converted by nitrous acid into naphthophenazine (Nietzki a. Otto, *B.* 21, 1598).

A di-methylated eurhodine

$C_{10}H_6.N_2.C_6H_3NMe_2$ $\left[\begin{matrix}1\\2\end{matrix}\,4\right]$ [205°] is formed by heating nitroso-di-methyl-aniline hydrochloride (3 mols.) with a solution of (β)-naphthylamine (2 mols.) in HOAc (Witt, *B.* 21, 719).

EUXANTHIC ACID $C_{19}H_{16}O_{10}$. *Purreic acid.* The magnesium salt constitutes the essential part of Purree or Indian yellow, said to be obtained by evaporating the urine of cows fed on mangoes (Stenhouse, *A.* 51, 423; Erdmann, *J. pr.* 33, 190; 37, 385; Baeyer, *A.* 155, 257). Purree is boiled with water and the residue extracted with dilute HCl; on cooling the euxanthic acid separates in stellate groups of needles. Euxanthic acid is also excreted in small quantity by a rabbit after taking euxanthone (Kostanecki, *B.* 19, 2919).

Properties.—Pale-yellow needles, containing aq when crystallised from alcohol, but 3aq when ppd. by HCl from its ammoniacal solution. It has a sweet taste and a bitter aftertaste. It is sl. sol. cold water, v. sol. boiling alcohol, m. sol. ether. Alkalis colour its solution deep-yellow. When cautiously heated at 170° it gives off water and CO_2, leaving a yellow sublimate of euxanthone. Alcohol and HCl also give euxanthone. HNO_3 gives tri-nitro-euxanthone and tri-nitro-resorcin. By heating with dilute H_2SO_4 (2 p.c.) at 140° it is split up into euxanthone and glycuronic acid (Spiegel, *B.* 15, 1965).

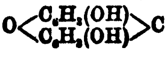
Salts.—The euxanthates of the alkalis are v. e. sol. water, but are ppd. by excess of alkaline carbonate. The euxanthates of Ba, Ca, and Mg are sl. sol. cold, v. sol. hot, water. The basic Mg salt which occurs in purree is insol. water.—NH_4HA''aq: light-yellow needles.—KHA''aq.—MgA'' 9aq?: occurs in purree.—$PbH_2A''_2$.—PbA''.

Di-bromo-euxanthic acid $C_{19}H_{14}Br_2O_{10}$. Minute golden-yellow needles (containing aq).

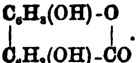
Di-chloro-euxanthic acid $C_{19}H_{14}Cl_2O_{10}$. Formed by passing Cl into water in which euxanthic acid is suspended. Golden scales; insol. water, v. sol. boiling alcohol. Its salts are mostly gelatinous.

Nitro-euxanthic acid $C_{19}H_{15}(NO_2)O_{10}$. From the acid and cold HNO_3 (S.G. 1·31). Straw-coloured laminæ (from alcohol).

EUXANTHONE $C_{13}H_8O_4$ *i.e.*



$O\!\left<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}\right>\!CO$ or more probably


$$\begin{array}{l} C_6H_3(OH)\text{-}O \\ | \qquad\qquad\quad | \\ C_6H_3(OH)\text{-}CO \end{array}$$
. [232°]. V.D. 8·0 (calc. 7·9). A product of the decomposition of euxanthic acid (Stenhouse, *A.* 51, 425; Erdmann, *A.* 52, 365; 60, 239; Schmidt, *A.* 93, 88; Graebe, *B.* 16, 864). It is produced by heating the acid or its Ba or Pb salt; by treating the dry acid with conc. H_2SO_4; or by treating its alcoholic solution with HCl. Pale-yellow needles or laminæ (from alcohol); v. sl. sol. water, v. sol. ether, sl. sol. alcohol (Külz, *Z. B.* 23, 475). It may be sublimed. It is neutral in reaction, dissolves in alkalis, but not in dilute acids. The alcoholic solution is ppd. by lead subacetate, but not by lead acetate, baryta, or lime. $FeCl_3$ gives a green colour. Does not react with hydroxylamine or with phenyl-hydrazine (Spiegler, *B.* 17, 808).

Reactions.—1. *Nitric acid* forms tri-nitro-euxanthone and tri-nitro-resorcin.—2. Passing over heated *zinc-dust* forms $CH_2{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}O$ and other products.—3. *Potash-fusion* gives hydroquinone and euxanthonic acid (Baeyer, *Z.* [2] 5, 569).—4. *Sodium-amalgam* gives a colourless compound which turns violet-black in the air (Wichelhaus a. Salzmann, *B.* 10, 1398).

Salts.—A″Mg: insol. water, nearly insol. alcohol.

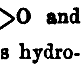
Methyl ether A″Me_2: [130°]; yellow needles or prisms, sol. alcohol and ether (Graebe a. Ebrard, *B.* 15, 1675).

Ethyl ether A″Et_2: [126°]; long colourless or yellow prisms, sol. alcohol and ether.

Acetyl derivative $C_{13}H_6Ac_2O_4$: [185°]; yellowish prisms (from benzene); sol. alcohol, sl. sol. ether.

Benzoyl derivative: [214°]; yellow crystals, sol. aniline, insol. alcohol, ether, benzene, &c.

Constitution.—Euxanthone is clearly a di-oxy- derivative of the so-called di-phenylene ketone oxide, but as this substance does not react with hydroxylamine, Spiegler suggests that it should be represented by the formula

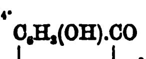

$$\begin{array}{l} C_6H_4.O \\ | \qquad\ | \\ C_6H_4.CO \end{array}$$

rather than $CO{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}O$.

Di-chloro-euxanthone $C_{13}H_6Cl_2O_4$. From di-chloro-euxanthic acid by dissolving in conc. H_2SO_4 and ppg. by water (Erdmann, *J. pr.* 37, 397). Yellow powder.

Tri-nitro-euxanthone $C_{13}H_5(NO_2)_3O_4$. From euxanthone and HNO_3. Minute yellow needles. Further treatment with HNO_3 gives tri-nitro-resorcin. NH_3 forms reddish-black grains of $C_{13}H_4(NH_4)(NO_2)_3O_4$.

Iso-euxanthone


$$\begin{array}{l} C_6H_3(OH).CO \\ | \qquad\qquad\ \ | \\ C_6H_3(OH).O \end{array}$$

. *Lactone* of *tri-oxy-diphenic acid.* [243°]. Obtained by heating di-oxy-benzoic acid (β-resorcylic acid) with acetic anhydride; the yield is about 4 p.c. (Bistrzycki a. Kostanecki, *B.* 18, 1986). Small needles. V. sol. alcohol, ether, and aqueous alkalis forming yellow solutions, insol. water. Sublimes in long yellow needles. Fe_2Cl_6 gives a greyish-green colour. The alcoholic solution gives a yellow pp. with $MgSO_4$. Treated with sodium-amalgam and water it dissolves with a blood-red colour.

EUXANTHONIC ACID $C_{13}H_{10}O_5$ *i.e.* $\left[\begin{smallmatrix}2\\5\end{smallmatrix}\ 1\right]C_6H_3(OH)_2.CO.C_6H_3(OH)_2\left[1\ \begin{smallmatrix}2\\5\end{smallmatrix}\right]$. *Tetra-oxy-benzophenone* (?). Formed from euxanthone by potash-fusion (Baeyer, *A.* 155, 259). Yellow needles (from water). Forms a reddish-yellow pp. $C_{13}H_6Pb_2O_5$ with basic lead acetate. Its solution in potash rapidly oxidises in the air, becoming dark. $FeCl_3$ colours it red. Resolved by heat into water and euxanthone, which sublimes. Boiling aqueous NH_3 also forms euxanthone. Potash-fusion converts it into hydroquinone (Graebe a. Feer, *B.* 19, 2607).

EVERNIC ACID $C_{17}H_{16}O_7$. [164°]. Obtained, together with usnic acid, by macerating the lichen *Evernia prunastri* with milk of lime and ppg. the filtrate with HCl; it is extracted from the dried pp. with boiling alcohol and ppd. by water (Stenhouse, *A.* 68, 83; *Pr.* 18, 222). Groups of small needles (from alcohol). Insol. cold water, v. sol. cold alcohol and ether. It does not decompose solutions of $NaHCO_3$ in the cold; its Ca salt is decomposed by CO_2. Decomposed by boiling with water or baryta-water into CO_2, orcin, and everninic acid.

Salts.—BaA'_2aq; small prisms, sl. sol. cold water, v. sol. dilute alcohol.—KA′: silky crystals, sl. sol. cold water, v. sol. dilute alcohol and aqueous KOH.

Tetra-bromo-evernic acid $C_{17}H_{12}Br_4O_7$. [161°]. From dry evernic acid and dry Br. Colourless prisms (from alcohol); insol. water and CS_2, sl. sol. hot benzene, v. sol. ether.

EVERNIIN $C_9H_{14}O_7$ (Stüde, *A.* 131, 241). A substance extracted from *Evernia prunastri* and related to the sugars. The plant is macerated with cold dilute soda-ley till the liquid acquires a dark-green colour; the filtrate is mixed with alcohol; and the brown flocks thereby precipitated are redissolved in water and purified by repeated precipitation and boiling with animal charcoal.

Everniin is an amorphous, yellowish, tasteless powder, which swells up in cold water and dissolves easily in hot water. Its aqueous solution gives with lead acetate and ammonia a pp. soluble in acetic acid. It is ppd. by a large excess of glacial acetic acid. It prevents the ppn. of lead by H_2S or sulphuric acid, a property likewise possessed by glycogen, inulin, lichenin, and gum. Everniin is not coloured by iodine. Dilute acids easily convert it into glucose.

A substance closely related to, or perhaps identical with, everniin is obtained from *Borrera ciliaris.*

EVERNINIC ACID $C_9H_{10}O_4$. [157°]. Formed by decomposing evernic acid with caustic alkalis (Stenhouse, *A.* 68, 86; Hesse, *A.* 117, 299). Best prepared by boiling evernic acid with baryta water; $BaCO_3$ is ppd., and the filtrate, treated with HCl, gives a pp. of everninic acid. Laminæ, sl. sol. cold, m. sol. boiling, water, v. e. sol. alcohol and ether. $FeCl_3$ colours its solution violet. Conc. HNO_3 forms evernitic acid $C_9H_8(NO_2)_2O_4$ or $C_9H_9(NO_2)_3O_2$? which forms pale yellow prisms, sl. sol. cold, m. sol. boiling water, and forms a crystalline potassium salt $C_9H_7K_2(NO_2)_3O_2$ ½aq? (Hesse). Evernitic acid is perhaps di-nitro-everninic acid. Everninic acid differs from evernic acid in not yielding orcin when boiled with potash.

Salts.—$Ba(C_9H_9O_4)_2$ 2aq: long four-sided prisms, nearly insol. alcohol.—AgA′: white pp.

Ethyl ether EtA′. [56°]. From evernic acid by boiling for 9 hours with strong alcohol, or with alcohol containing KOH. Long colourless crystals (from alcohol), insol. cold, nearly insol. boiling, water, v. sol. alcohol and ether. Dissolves in aqueous KOH but not in aqueous NH_3 or K_2CO_3.

EXCREMENT. Berzelius (*Lehrbuch*, [4] 9, 340) found in human fæces: water, 75·3 p.c.; bile, ·9 p.c.; albumen, ·9 p.c.; soluble organic matter, 2·7 p.c.; salts, 1·2 p.c.; insoluble residue of digested food, 7 9 p.c.; insoluble organic matter (mucus, bile-resins, and fat), 12 p.c. Human excrement, acidified by H_2SO_4, yields on distillation acetic, *n*- and *iso*-butyric, valeric and caproic acids, phenol, indole, and skatole (from σκατός = fæces) (Brieger, *J. pr.* [2] 17, 124). *V.* also Wehsarg, *Untersuchung. der Fæces*, Giessen, 1853; Porter, *A.* 71, 109; Fleitmann, *P.* 75, 356; Marcet, *T.* 1854, 265; 1857, 403; *C. J.* 10, 162; Harley, *Pr.* 7, 122.

Thenard (*C. R.* 44, 980) found in fermented manure an acid $C_{30}H_{30}N_2O_{10}$, which may be ppd. from an aqueous extract by HCl. It is a black mass, insol. water, v. sl. sol. alcohol and ether.

EXCRETIN $C_{20}H_{36}O$ (Hinterberger, *A.* 166, 213; *cf.* Marcet, *Pr.* 9, 308). Obtained by exhausting fresh excrements with boiling alcohol and leaving the solution to stand for a week. A black pp. then separates out, containing excretin and the salt $C_{56}H_{113}MgNO_{11}$. The filtrate is ppd. with milk of lime, and the dried pp. treated with a hot mixture of ether and alcohol. On exposing the solution during a week to a temperature below 0°, crude excretin crystallises out in semi-globular masses consisting of yellow needles. It is purified by crystallising it repeatedly from alcohol, with addition of blood-charcoal, the temperature being kept below 0°. Bromine converts it into di-bromo-excretin, $C_{20}H_{34}Br_2O$, which separates from a mixture of ether and alcohol in hard brittle crystals grouped in globular masses. A crystalline chlorine-compound could not be obtained. 100 pounds of fresh excrements yielded 8 grams of pure excretin.

EXPLOSION. If a system is in such a condition of physical or chemical equilibrium that a variation of that condition involving a transformation of energy, and initiated at any one point, will spread rapidly through the system of its own unaided action and without the supply of energy from without, then the system itself is said to undergo explosive change, and the change itself is called *explosion*. If the velocity of change is small the explosion becomes a combustion; if large, a detonation.

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From considerations of economy of space the following account of the vast mass of work which has been done in connexion with the theory of explosions has been compressed as much as possible.

Explosion of Gases.—First really studied by Davy, and leading to the invention of the safety lamp; afterwards by Bunsen, Horstmann, Berthelot, Vieille, Sarrau, Mallard and Le Chatelier, Dixon, Clerk (*Gas Engine*, Longmans, 1887), and Von Oettingen and Von Gernet. The latter found (*W.* 4, 1888) that when a eudiometer tube is filled with water-gas ($H_2 + O$) and explosion is induced by an electric spark, the luminosity is sufficient to enable a photograph to be obtained when the dust of some copper salt is distributed in the tube. By an ingenious combination of apparatus the flash can be reflected from a rotating plane mirror, and a real image of the analysed phenomena thrown on a sensitised plate (Eastman's negative) contained in a camera. It appears from a study of the picture obtained that the explosion is really very complex. The photographically active illumination does not occur till ·001 sec. after the passage of the spark, this represents the time required for the copper salt dust to become luminous. The explosion, however, is shown to be practically over by this time. The photographs show waves of compression (indicated by excessive luminosity) to be travelling up and down the tube. There is also some indication (not convincing) of successive partial explosions taking place at periods of about ·0001″ to ·0002″. Bunsen has suggested (*P.* 1867) that the temperature at first attained is so high as to prevent complete combination, or in other words to cause dissociation of steam, and that as cooling takes place a number of secondary explosions occur until the combination becomes complete. These supposed successive explosions are indicated by secondary wave-markings in the photograph. The explosive velocity appears to be about 2,800 metres per second, and the velocity of the pressure waves about 600 metres per second. If the temperature reaches 3000°C., as indicated by Berthelot, sound would travel through the gas with a velocity of 1,150 metres per second; the result therefore shows (assuming the reasons given for identifying the observed wave with waves of compression to be valid) either that 3000°C. is far too high a temperature, or that the displacements in the wave motion are such that the velocity is less than the velocity of sound, which is unlikely. Probably the conditions are such as to preclude any comparison with the velocity of sound under ordinary conditions; even supposing the adiabatic condition to be really fulfilled (but from the mere fact of the possibility of photographing we know this cannot be the case) there is room for great speculation as to the value of γ. Again, Kundt finds that powder in the tube has considerable effect even with small disturbances, and that in narrow tubes the velocity diminishes both with the diameter of the tube and with the wave length of sound (*v.* Rayleigh's *Sound*, vol. 2, pp. 26-54). Besides all this, the displacements are probably so large as to render the ordinary equations unavailable. The whole of the photographically luminous phenomena are over in ·004 seconds. These researches, however, require confirmation.

The further stages have been investigated by other philosophers. In 1867 Bunsen published an account of some experiments he had made to determine the maximum pressure due to an explosion as well as the velocity with which explosion proceeds in gases. By estimating the heat produced during any explosion—which may be done from thermo-chemical data—and assuming that the specific heat of the products of combustion is either constant, or varies in some assumed way, it is clear that the maximum pressure produced may be calculated by assuming Boyle's Law or any modification of it—of course on the further assumption that no heat is lost from the exploding mixture before the maximum pressure is attained. Bunsen found that in certain explosive mixtures tested by him the theoretical pressure was never even approximately attained. The pressure gauge in Bunsen's experiments consisted of a sort of safety valve loaded to a known extent. Now it is clear, from the study of the equation of motion of such a valve, that much will depend on the period during which it is subjected to the high pressure; in fact to get a satisfactory result we ought to take into account the period of time during which the gases are rising to their real maximum of pressure. This period was an unknown quantity till Sarrau a. Vieille and Berthelot determined it about twelve years later. However, Bunsen concludes from his experiments that the reason for the calculated maximum pressure not being attained in his apparatus is to be sought in the dissociation or rather postponed combination of the explosive gases. Bunsen also attempted to measure the velocity of combination by allowing the mixed gases to stream out by a narrow hole, and finding the least possible velocity which would prevent explosion running back into the reservoir. The assumption made is that when the velocity of efflux equals or exceeds the velocity of explosive propagation the flame will not run back. This we know cannot be true because of the conductivity of the material through which the jet passes; and besides this there is the cooling of the jet by expansion to be considered, tending to cause the rate of combination thus obtained to refer to gases at an undiscovered temperature. For water-gas Bunsen got a velocity of 34 metres per second, and for a mixture of equal volumes of carbon monoxide and oxygen he obtained the rate of one metre per second at atmospheric pressure. Mallard and Le Chatelier (*A. M.* 8, [1871]) show that for different mixtures the velocity becomes much smaller if an excess of one component is employed, or if an inert gas be present; they also show that much depends on the mode of inflammation. With the chemical ideas we shall have to deal later on. The real measure of the velocity, as well as of the later phenomena of combination, we owe to Dixon (*T.* 1884, 'On Conditions of Chemical Change in Gases'), to Sarrau and Vieille, and to Berthelot (Berthelot, *Traité sur la force des matières explosives*). The works in question are happily easily accessible, and therefore a mere summary will suffice here:—

1. The initial velocity of explosion depends on the diameter of the tube, on the pressure of the gases, on the initial mode of inflammation, and on the temperature of the mixture.

2. If the pressure is not too low and the diameter of the tube not too small, the reaction velocity will be accelerated, and will finally rise to a certain value which is henceforth pretty constant.

3. This velocity is independent of the nature of the material of the tube, and of its length, provided this is above the 'critical value' required to enable the so-called explosive wave to get established. The same remark applies to the diameter of the tube.

4. The velocity of the explosive wave does not depend on the pressure between the limits investigated, nearly to an atmosphere.

5. The influence of the chemical nature of the mixture is difficult to estimate, because in varying the composition, the disengagement of heat, and consequently the maximum temperature, varies. In fact the velocity approaches the velocity of molecular motion (of translation) calculated by Clausius and given by his formula

$$V = 29{\cdot}354\sqrt{\frac{T}{\rho}}$$

where T is absolute temperature on the thermodynamic scale, and ρ is the density of the gas referred to air (it is the density of the products of combustion that should be taken, but as unknown dissociation intervenes this is often difficult to estimate). The approximate agreement of this formula with the observed velocity suggests that very possibly it may afford a better means of measuring the real absolute temperature in the explosive wave than the thermochemical data actually employed. For although the same uncertainty exists as to the value of ρ we need make no assumption as to the specific heat of the gases at the high temperature attained.

6. The explosive wave may be initiated at once by using a suitable detonator of mercury fulminate. Berthelot used fulminating electric interrupters to obtain registration on his chronograph. Dixon used similar interrupters without the fulminate, and found that Clausius' formula gave good results when the gases were wet. In fact the dryness or wetness of the gases is important for most mixtures, but not for water-gas. Berthelot and Vieille used a falling rod chronograph, Dixon a myograph. Dixon finds that in mixtures of carbon monoxide and oxygen the reaction products depend on the velocity of explosion, *i.e.* on the temperature obtained; carbon may even be deposited at high velocity. Similarly Berthelot and Vieille succeeded in completely decomposing acetylene into carbon and hydrogen by starting the wave with mercury fulminate. Finally Sarrau and Vieille (*C. R.* 105, 1222-4) find that the final equilibrium in many exploded gaseous mixtures depends on the pressure obtained; which in turn depends on the density of charge. Density of charge is defined as

$$\frac{\text{charge in grams}}{\text{vol. available for explosion in cubic centimetres.}}$$

The following table will give an idea of the results obtained by Messrs. Berthelot and Vieille; the remarks are from Dixon's paper:—

Mixture	Sp. Grav. of products	Theoretical temperature absolute	Velocity calculated	Velocity found	Remarks
H_2+O	·622	5780°	2831	2810	Wet or dry.
$CO+O$	1·529	6700°	1941	1089	Dry; when wet agrees better.
C_2H_2+5O	1·227	1007°	2660	2482	
$C_2H_4+3O_2$	1·075	7880°	2517	2209	
$C_2N_2+2O_2$	1·343	9650°	2490	2195	Does not explode dry at ordinary pressures.

Mach and Wentzel (*W.* [1885] 26, 628) have investigated the velocity of decomposition of silver fulminate piled in a heap in free air. This they did by an ingenious method of firing two linear parallel heaps of fulminate on, or at the edges of, a plate of smoked glass. The heaps of fulminate were of equal length and were ignited simultaneously at opposite ends by the discharge of a Leyden jar. On examination, the smoked glass showed markings due to the motion of the air caused by the explosion. The authors note particularly a line which appears to be straight and inclined at an angle to the parallel heaps. This is supposed to be the line representing the locus of points of equal time with respect to the detonating heaps. If the velocity of the considerable aerial disturbance be taken at 400 metres per second, then by Huyghens' principle

$$V = \frac{400}{\sin\alpha} \text{ metres per second,}$$

where V is the velocity of ignition sought for. An experiment gave V>1,700 metres per second and <2,000 metres per second.

Notes as to chemical changes.—Bunsen, experimenting with a mixture of carbon monoxide, hydrogen, and oxygen (too little for complete combustion), concluded that the ratio of water to carbon dioxide formed did not vary continuously, but by sudden jumps. Bunsen also found that the more rapid the combustion the more water and the less carbon dioxide was produced. Horstmann, by using pretty long tubes, got numbers from which he deduced a theory of the coefficient of affinity. Dixon discovered that for uniform results it is necessary that the pressure should be above the 'critical pressure.' This 'critical pressure' is the pressure beyond which length of tube has no effect on the result; it is higher the less explosive is the mixture. For instance, wet carbon monoxide with 12 p.c. of free oxygen has a 'critical pressure' of 400 mm.; if there is 19 p.c. of oxygen the 'critical pressure' falls to 200 mm. The 'critical pressure' is then the pressure above which the true explosion takes place. When the pressure is above the 'critical pressure,' and when the products of combustion are prevented from leaving the sphere of action by condensation or otherwise, and no inert gas is present to lower the temperature, and there is less hydrogen than twice the volume of the oxygen, then the coefficient of affinity (to be defined below) remains constant and is equal to 4; or in other words the ratio of burnt to unburnt gas is constant. A typical case is a mixture of carbonic oxide, hydrogen, and oxygen.

Direct actions are $\left.\begin{array}{l}2H_2+O_2=2H_2O\\2CO+O_2=2CO_2\end{array}\right\}$;

reverse actions are $\left.\begin{array}{l}H_2O+CO=H_2+CO_2\\H_2+CO_2=H_2O+CO\end{array}\right\}$.

If H is the number of molecules of steam, H′ the number of molecules of hydrogen, K′ the number of molecules of carbon monoxide at the beginning of the reaction, and K the number of molecules of carbon dioxide at the end of the reaction, then $\frac{K'H}{KH'} = \alpha$ the coefficient of affinity.

For real information on these points the paper must be consulted. We can also do no more than refer to the very important experiments made by Mallard and Le Chatelier on the pressure produced by gaseous explosions (*A. M.* [8] 4, 272 [1883]). These philosophers used a Bourdon gauge indicator, and obtained a diagram showing the rate of cooling of the gases of explosion. The experiments of Clerk (*l.c.*) were directed to the practical application of gaseous explosions in gas engines; his apparatus consisted of a Richards' indicator with a drum travelling at constant speed; and his results are of a definite practical importance.

LIQUIDS AND SOLIDS. *General phenomena.*—For purposes of convenience the solid explosives are generally divided into two classes: one typified by gunpowder, the other by detonated gun-cotton. The first class is for the most part occupied by explosive mixtures; the second by explosive compounds. An accurate practical distinction may be made between those substances in which detonation may be produced as easily as in gun-cotton, say, and those in which it cannot be so easily produced. The general phenomena common to both classes of explosives are:—

1. A rapid chemical change attended by in-

crease of volume and production of heat (this excludes such cases as the action of tartaric acid on sodium carbonate where heat disappears).

2. A dependence of the rate, and hence generally of the nature, of the decomposition on the greater or less facility which the products have for escaping from the seat of the reaction. This information we owe to Abel.

3. If the substance is inclosed in a confined space the final pressure of the products will depend on the ratio of the volume of the space to the volume of the explosive substance; on the heat produced during the reaction; on the nature of the reaction as influenced by the escape of the products; on the greater or less dissociation of the products; on the physical state (solid, liquid, or gaseous) of the products at the temperature of the explosion; on the relation of the velocity of cooling to the velocity of the reaction; and finally on the mode of inflammation in relation to the initial temperature.

We may at once premise that explosives of the second class differ essentially when 'detonated' from explosives of the first class, in that their reaction is analogous in point of velocity and means of propagation to the explosive mode of 'decomposition' observed in gases by Berthelot and Dixon.

It is immaterial whether the reaction by detonation or explosion of the 'first order,' as it is sometimes called, is brought about by a detonator of some other sudden explosive, or whether it is produced by the gradual rise of temperature and pressure produced by the products of the decomposition of some other part of the same mass. A detonation of gun-cotton may be produced equally well by using a detonator of confined fulminate of mercury, and preventing the escape of the products of combustion, or by igniting a portion of the gun-cotton by the application of a hot body or flame.

Many substances detonate or not according to the circumstances in which they are placed. Fulminate of mercury, for instance, piled in small quantities on a sheet of iron may be inflamed by a wire laid on the top without producing a much greater explosion than would be produced by gunpowder under similar circumstances. If the wire is placed beneath the heap and heated by a current to a sufficient temperature the slight resistance to the escape of the products of combustion first formed will be sufficient to convert the puff into a loud detonation, which bruises the plate.

It is very easy to get the explosive wave established in fulminate of mercury, and in fulminate of silver and iodide of nitrogen it is difficult to prevent it becoming established. (In some of Abel's experiments on the transference of exploding influence through tubes it was noted that the fulminate of silver did not explode with its usual violence.) In the nitroglycerin compounds the relative ease or difficulty of establishing an explosion of the first order, *i.e.* detonation, depends largely on the physical state of the substance. In all cases what is required is that the pressure on, and the temperature of, a portion, no matter how small, of the substance to be exploded, shall rise above a certain critical value which depends on the nature, initial temperature, and physical state, of the substance. It is not necessary to make any hypothesis such as that long since suggested by Abel as to 'synchronism of vibration,' the anomalies which it was framed to account for having either arisen from misapprehension, or having been accounted for in other ways.

We proceed to the general theory.

Provided the reaction is complete the heat given out may be obtained from the thermochemical data which we owe to Berthelot. A little care is requisite here, because it generally happens that some of the products of combustion are liquid at ordinary temperatures. Now if we wish to determine the maximum pressure, this will involve a knowledge of the heat of combustion when all the products are kept gaseous. Sometimes it may happen that a reaction taking place at high velocity is not identical with that at the velocity actually attained in the necessary calorimetric experiments. In such cases we must make sure (by analysis of the products) either that the reaction has not changed, or if it has, due allowance must be made in the thermochemical data. A much greater difficulty arises in estimating the percentage of combination which has occurred when the maximum pressure is reached. We may either introduce a correction (if one is to be found) in the data for the heat of reaction, or in the data for the specific heat of the products. It will be convenient to assume, with the higher explosives at all events, that the maximum pressure is reached before any heat is lost to the containing vessel. It will also be important to note that a decomposition-reaction taking place at constant volume may not be identical with the reaction at constant pressure. With the higher explosives the reaction even in the open air is more nearly at constant volume than at constant pressure.

If Qv is the heat of the reaction available for raising the temperature of the products at constant volume, and Qp is the corresponding number at constant pressure, and if the volume of gas liberated is known, then $Qv = Qp +$ thermal equivalent of work done in overcoming external pressure. For instance, for 227 grms. of nitroglycerin Qp will be 356·5 kilogram-degrees, and Qv 360·6 kilogram-degrees. The volumes of the gases of combustion being supposed to be reduced to 0° and to expand against a pressure intensity of one atmosphere, Qv comes to 1,590 gram-degrees per gram of nitro-glycerin at an initial temperature of 15°C. Sarrau and Vieille found by a calorimetric experiment 1,600 gram-degrees. To take a simple case: Suppose the thermal value of the reaction (Qv) can be obtained for a gram of substance, let this quantity of substance be inclosed in a space of v c.c., and suppose its own volume negligibly small in comparison; let the products of reaction, supposed still gaseous and obeying Boyle's Law, occupy a volume v' at 0° and 760 mm.; let the specific heat of the product supposed constant be σ, and let m represent the ratio of the portion burnt to the whole initial amount at the epoch of maximum pressure P, then the formula will become

$$P = \frac{v'}{v} Qv \frac{m}{\sigma}.$$

Now it is clear that as this calculation is based on Boyle's Law, the temperature being considerable, we must expect a merely approximate result, according to Amagat's experiments at high temperatures and pressures. Again our knowledge of σ, a quantity which is possibly dependent on the pressure and temperature, is mere guess work, and the same may be said for m. The only at all satisfactory case is that of fulminate of mercury ($HgC_2N_2O_2$), the products being 2CO and N_2, a mixture not very susceptible of dissociation, though Dixon noted that even CO is decomposed at high velocities. Berthelot shows that the effect of dissociation is in all cases to lower the pressure, the heat used being without exception insufficiently compensated by the increased volume of the gas liberated. For speculation as to the probable value of P from theoretical considerations the reader is referred to Berthelot. We shall describe the practical way in which the pressure is measured, and content ourselves with pointing out that Berthelot's theory leads to results which sometimes (according to his success in guessing m and σ) do not differ widely from the experimental results. Of Berthelot's experiments it is impossible to speak too highly.

The instrument used in measuring pressures is based on the crusher gauge invented by Rodman, and improved by Noble and by Abbot; the former by the introduction of a cylindrical crusher and copper cylinder, the latter by the addition of a clutch making its use possible under water. For our purpose the best experiments are those of Sarrau and Vieille, for to them belongs the honour of having rightly interpreted the indications afforded by the gauge. The difficulty of interpretation will be best understood after a short description of the normal type of crusher. This instrument consists essentially of a hollow cylinder of mild steel, strengthened, if necessary, externally by winding with wire. The cylinder is open at one end and closed at the other by a strong screw plug; the explosive to be investigated is placed in the hole and usually rests near the plug; the electrical firing arrangements pass through the plug itself. The capacity of the instrument used by Sarrau and Vieille was about 24·33 c.c., and the diameter of the bore was 2·2 centim. A ram piston is inserted into the open end of the bore, and is supported at its outer end by a cylinder of pure copper, which in turn rests on a massive anvil braced to the rest of the apparatus. The instrument is strengthened by two plates, one at each end, braced together by strong bolts. The dimensions of the soft copper cylinder are accurately determined by a previous experiment, and the charge is weighed and introduced below the plug, the volume of the bore down to the piston head being accurately measured. On firing, the increase of pressure due to the explosive gases causes the piston ram to 'crush' the copper cylinder. The problem is to find the maximum pressure exerted on the cylinder. In Rodman's instrument the piston was furnished with an indenting tool, and the apparatus itself was of slightly modified construction, being screwed into a gun and the piston being acted on directly by the explosion of the gunpowder when the gun was fired. Rodman's interpretation was based on experiments made with a testing machine. His assumption was that the dimensions of the 'cut' of the copper depended on the maximum pressure; the calibration was effected by producing an equivalent cut in a testing machine and measuring the pressure at which it occurred.

This is rightly criticised by Abbot, who adopts a rather different method. He uses a solid cylinder of lead and crushes it by means of a flat-headed piston. If the length changes during the operation from L to L′, and if F is the mean resistance of the lead cylinder to deformation, then the work done is

$$W = F(L - L').$$

W is next measured by the fall of a hammer head pendulum. The distance through which the pendulum falls is so arranged that it produces the same crush as that observed in an experiment. In Abbot's case the pressures measured were pressures of explosion under water, and his apparatus therefore more resembled Rodman's. The kinetic energy of the blow being known, and the assumption being made that all the energy is effective in producing the crush, or, what comes to the same thing, that the effectivity is the same during the hammer-blow (he does not say this) as it is during the experiment—we have a means of obtaining in the first case an absolute measure of W; in the second[1] a measure proportionate to W.

It is clear, therefore, that if the resistance is a known function of the length we shall be able to obtain a value for F leading to a true result. As a matter of fact the process of 'crush' is complex, the resistance being very different before and after flow takes place.

It is probable that in the immense deformations employed by Abbot the chief resistance is resistance to flow, and this will to a certain extent depend on the velocity of flow. In other words, his calibration is inexact unless the piston of the crusher moves with the velocity of the hammer.

The explosion endues the piston with kinetic energy, and this energy is spent in deforming the cylinder. It is clear at once that much will depend on the time required for the pressure to reach its maximum considered in connexion with the mass of the piston. Sarrau and Vieille (*C. R.* 95, 26, 130) use copper cylinders in connexion with the instrument described above. The equation of slow crush in the testing machine is

$$T = K_0 + K\epsilon,$$

ϵ being the crush, or change of length produced, K_0 and K constants, and T the pressure producing the observed crush. If the crush is not very great, and the rate of crush slow, K seems fairly constant up to pretty high values. It by no means follows, however, that the case is the same if the velocity of flow be great. When the cylinder is crushed by one explosion two extreme cases have to be considered.

1. The piston may be so light that the pressure of the explosion is transferred to the copper cylinder practically at the time of its development in the explosion cylinder.

2. The explosive pressure is so rapidly produced, or the piston is so heavy, that the maxi-

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[1] Of course in the end all the energy, or nearly all, is converted into heat in the cylinder and neighbouring surfaces.

mum pressure is reached *before the piston begins to move.*

In practice of course there are intermediate cases. Let $p=f(t)$ be the variable pressure at the base of the piston, m the mass of the piston, R the resistance of the cylinder, u the displacement of the piston after time t. Neglecting the compression of the piston, &c., the equation of motion is

$$m\frac{d^2u}{dt^2}+\mathrm{R}=f(t),$$

within the limits $\mathrm{R}=\mathrm{K}_0$ to $\mathrm{K}u$. Neglecting the work done within the elastic limits of the cylinder, and taking care that the charge is of such a size as not to cause the crush to pass the limit for which the equation holds, this becomes

$$m\frac{d^2u}{dt^2}+\mathrm{K}_0+\mathrm{K}u=f(t).$$

This may be integrated, and when the pressure passes through its maximum P, we get a relation between this maximum and the final crush of the cylinder. This solution is of the form

$$\mathrm{P}=\mathrm{K}_0+\frac{\mathrm{K}\epsilon}{1+\phi\left(\frac{t}{t_0}\right)},$$

t being the time from the origin to the epoch of maximum displacement, and t_0 the period of crush of the cylinder under a constant force acting without initial velocity through the mediation of a piston of equal mass m; ϕ is such a function that it is unity when the variable vanishes, and decreases rapidly as the variable increases. So the value of P depends on our knowledge of $\frac{t}{t_0}$, and this must be determined in each case.

Now, t_0 is given by

$$t_0=\pi\sqrt{\frac{m}{\mathrm{K}}};$$

it is the period (or, as we should say, half period) of the piston. t is got by actual measurement: this is accomplished by allowing the piston to carry a style pressing on a chronograph drum.

In a general way the ratio is found to vary according to the mass of the piston employed. Sarrau and Vieille, however, prefer so to vary the mass of the piston that one or other of the extreme conditions is fulfilled. If the pressure rises slowly (within the sense of the equation) then

$$\mathrm{P}=\mathrm{K}_0+\mathrm{K}\epsilon.$$

If, on the other hand, the piston moves under constant force,

$$\mathrm{P}=\mathrm{K}_0+\frac{\mathrm{K}\epsilon}{2}.$$

Some interesting cases present themselves. When $\frac{t}{t_0}$ varies between 4·8 and 251, the crush remains the same (or nearly so) with powder, showing that with the piston used the first equation must be employed. With potassium picrate, on the other hand, no sensible value can be assigned to t, and the second condition is fulfilled. The same remark applies to gun-cotton and fulminate of mercury; with dynamite, on the other hand, we have an intermediate case. The first condition is wholly unattainable in practice, and the second only when the mass of the piston is very great (in the experiments of Sarrau and Vieille it was 4 kilos.). If the piston had a mass of from 3·8 to 6·9 grs. only, then the crush for a given quantity of dynamite was only half what it was when the crush was given by the heavy piston; for intermediate values of the piston weight the crush was also intermediate.

With the exception, therefore, of the difficulty above mentioned as to rate of crush, we may consider that Sarrau and Vieille's experiments establish the right of the crusher to consideration as an instrument of precision. It must not be forgotten, however, that the indications afforded refer to mean maximum pressures only. There may be much local variation at points near the centre of explosion. By considering the nature of the possible means of escape of the gaseous products, it appears that vortex motion and jet motion may be set up. This was noticed by Threlfall (*P. M.* 1886) in the case of small explosions of fulminate of mercury under water, by Abbot in the case of large submarine dynamite explosions, and by Berthelot as a result of his general experience. The latter notes that metals subjected to the influence of detonating compounds are 'creusés et sillonnés,' and referring to the seat of such explosions he remarks: 'En realité, les gaz brusquement developpés par la réaction chimique représentent de véritables tourbillons, dans lesquels il existe des filets de matière sous des états de compression très différents, et une fluctuation intérieure.'

It will be evident that there is much difficulty in answering such a question as 'What is the strongest explosive?'—in fact, no answer can be given unless the conditions of explosion are specified. We may arrange explosives in the order of maximum pressures developed per unit mass in unit volume in a crusher gauge, or we may construct a table showing the pressures produced by unit masses in their own volumes, or by equal volumes in their own volumes. For instance, in the case of fulminate of mercury with an actual density of charge at the rate of 3 g. per c.c., the crusher indicates a pressure intensity of about 6,000 kg. per sq. centim. for unit density (the standard condition). For cotton-powder the figure mounts to 10,000 kg. per sq. centim. If, however, we consider equal masses of these substances exploding in a space just capable of containing them, the mercury fulminate (thanks to its specific gravity of 4·42) will produce the enormous pressure of 27,000 kg. per sq. centim., while the number for the cotton powder will be only slightly increased. Now detonators in practice consist of confined charges in copper or tin tubes, and therefore it is clear at once why fulminate of mercury is the detonator *par excellence*, even though the energy expended per unit mass is surpassed by other explosives. The period of the attainment of the maximum pressure of detonating substances, excepting nitro-glycerin compounds, may be taken as less than $\frac{1}{10000}$th of a second.

Fulminate of silver, though so remarkable as a violent explosive, fails as a detonator through lack of density. The peculiarity of it, and of iodide of nitrogen, lies in the ease with which the explosive wave can be established in them, rather than in the energy run down by a given volume, which is the practically important point. With respect to the uncertainty in the method of calculation referred to at the beginning of this article, it seems as if the very high temperature in the crusher gauge tends to counteract the uncertainty produced by the enormous pressures. We give the following example of the actual calculation in the case of fulminate of mercury:—

The heat of formation of

$C_2N_2O_2Hg$ (= 284) is 114,500 gram-units.

Deducting the heat of vaporisation of mercury, this comes to 114,500 − 15,400 = 99,100 units available. Taking 4·8 as the molecular specific heat at constant volume of the mercury vapour, the carbon monoxide, and the nitrogen, and neglecting the difference between this value and the value for liquid mercury, then

$$T = \frac{99{,}100}{4 \times 4{\cdot}8} = 5{,}161^\circ.$$

The volume of gas formed (CO + N) reduced by the ordinary assumption to 0°C. and 760 mm. will be 22·32 litres. At a temperature 5161° (taking into account the volume of gaseous mercury) we shall have under normal pressure

$$V = 89{\cdot}28\left(1 + \frac{5{,}161}{273}\right)$$
$$= 1{,}776 \text{ litres}$$

as the quantity of gas given off by 284 g. of fulminate in a certain crusher experiment.

Now, 10 g. of fulminate were actually fired in a space of 50 c.c.; the corresponding space for 284 g. would have been 1·42 litres, so by Boyle's Law the pressure would be

$$\frac{1{,}776}{1{\cdot}42} = 1{,}251 \text{ atmos.}$$

or 1,293 kg. per sq. centim.

The experiment in the crusher gave $\epsilon = 2{\cdot}4$ mm., and the time of reaching the maximum was negligible. Therefore (the constants being previously known)

$$P = 641 + 535$$
$$= 1176 \text{ kg. per sq. centim.}$$

Comparing these two numbers we get an idea of the closeness of the results; they agree to within about 10 p.c. The deviation may be due either to the error introduced by the flow of the copper or by any of the assumptions in the theory. The gauge-estimate is probably the more correct.

The following notes may be of service. It is well known that many of the more rapid explosives do not require any tamping—*i.e.* a charge of gun-cotton simply laid on a rock will do nearly as much work in breaking and shattering as if it were covered with sand or clay-tamping. The reason is that the increment of volume tends to take place with greater velocity than that with which sound is propagated through air. Consequently it may happen that the pressure rises above the crushing strength of the rock, in which case fracture will result. In order to produce any appreciable effect at all the velocity of explosion must be above some critical value; when this is surpassed the amount of destruction performed will depend on the energy available.

It is a well-known fact that a small charge of fulminate of silver fired on a card or thin sheet of glass will in general blow a hole through the card or glass without doing other damage. The cause of this phenomenon has been sought by several observers, the most reasonable of whom appear to be Mach and Wentzel (*l.c.*), who begin by showing that the same effect can be observed in a vacuum. This leads them to measure the velocity of escape of the gases formed during explosion, by observing their effect on hollow cups forming convenient portions of a ballistic pendulum. The resulting velocity turns out to be between 3,500 and 17,500 metres per second, with a probability that the lower limit is the one most nearly approached. The authors argue that the density of the gases evolved with this velocity must be very considerable, and hence that the effect on an obstacle must be comparable with the effect produced by the impact of a projectile. This leads to the interesting question of what occurs when a soft body is caused to penetrate a hard one in virtue of its high velocity, as when a tallow candle or bit of soft wood is shot through a door.

The so-called 'sympathetic explosion' of charges probably does not exist. Cartridges both of gun-cotton and dynamite may be shattered to dust by an explosion without being ignited. Detonation may be produced equally well in chemical compounds and in mixtures, such as that of dinitrobenzene and potassium chlorate; in either case all that is required is that the pressure and therefore the temperature should rise to a sufficient value at any one point of the mass.

The ease with which detonation may be brought about will depend *ceteris paribus* on the physical state of the explosive as to hardness, fluidity, &c. The most powerful—*i.e.* energy-liberating—explosive per unit volume is fulminate of mercury; the most powerful per unit mass is blasting gelatine (92 p.c. nitroglycerin and 8 p.c. nitrocellulose [the exact composition of the particular nitrocellulose is not stated]). The latter, owing perhaps to its physical state, is most difficult to detonate except in hard rock. For detailed information on matters connected with explosions the reader is referred to Berthelot. E. T.

F

FAGINE. An alkaloid said to occur in beech-nuts (Buchner a. Herberger; Habermann, *C. C.* 1884, 789; *J.* 1884, 1445).

FAT. The term fat was originally applied to all compounds of carbon, hydrogen, and oxygen, which leave a permanent grease-stain on paper. They were divided into solid fats and fatty oils, the latter being subdivided into drying and non-drying oils. Chevreul showed that most natural fats are mixtures of oleïn, stearin, and margarin, the last body being subsequently proved by Heintz (*A.* 80, 293; 84, 297) to be a mixture of stearin and palmitin. Chevreul also showed that on boiling with potash the potassium salts of oleïc, stearic, palmitic, or other acids, are formed as soaps, while glycerin is in most cases also produced. Chevreul classes paraffin and cholesterin as unsaponifiable fats, the other fats being saponifiable. The term fat is, however, usually confined to saponifiable bodies.

Preparation.—Fat is obtained from animal tissue by melting at 100°. The membranous portions may be removed by adding 1 pt. of very dilute HCl (containing ·03 pts. HCl of S.G. 1·12) to every 10 pts. of the raw fat, and heating in a water-bath (Pohl, *D. P. J.* 201, 254). The rancid odour often acquired by keeping is due to volatile fatty acids, which may be distilled off in steam by boiling with water (Dubrunfaut, *C. R.* 72, 37). The odour may also be removed by treatment with aqueous Na_2CO_3. Vegetable fatty oils are expressed from seeds; a second quantity may be got by grinding up the seeds and pressing them a second time while hot. Nitrogenous substances are removed from the oil by shaking with 1 p.c. conc. H_2SO_4. Fats are also extracted from animal and vegetable products by benzene.

Properties.—Solids or liquids, lighter than water, cannot be distilled. Insol. water, v. sol. ether, CS_2, benzene, and light petroleum; sol. alcohol. When strongly heated they give off a pungent odour of acrolein. Alcoholic NH_3 slowly converts the fats in the cold into glycerin and amides of the acids (Rowney, *J. pr.* 67, 157). Nitric acid oxidises fats, forming oxalic, succinic, and adipic acids. Nitrous acid causes oils which contain oleïn to solidify through the isomeric change of that liquid to solid elaïdin.

Saponification.—Fats are broken up into glycerin and fatty acids by treatment with superheated steam, or by boiling with aqueous alkalis with water and PbO, or with dilute H_2SO_4 (*cf.* Benedikt, *M.* 9, 518). Saponification may even be effected at 45° by agitation of the melted fat with aqueous NaOH containing NaCl (Mège-Mouriès, *C. R.* 58, 864; Legrand, *D. P. J.* 186, 151; Knapp, *D. P. J.* 180, 309; 192, 498; *cf.* De Milly, *D. P. J.* 186, 145). Saponification may be conveniently effected by heating with lime (3 p.c.) and water at 172°, or with H_2SO_4 (8 p.c.) at 115°, glycerin being distilled off with superheated steam.

Drying Oils.—These oils become solid through atmospheric oxidation. This tendency is increased by previous boiling with PbO. Linseed oil is the chief drying oil; it contains glyceryl linoleate.

Estimation.—The amount of fat in a mixture is determined by extracting with ether, and evaporating the extract. The amount of free fatty acid may be determined by titration (Stohmann, *J. pr.* [2] 24, 510; Hausamann, *Fr.* 21, 447; Gröger, *Fr.* 22, 289; Krechel, *Fr.* 23, 261). The molecular weights of the higher alcohols and of the oxy- acids present in fats have been determined by forming their acetyl derivatives and then saponifying these bodies by alcoholic potash and titrating the excess of potash, using alcoholic phenol-phthalein as indicator (Benedikt a. Ulzer, *M.* 8, 41).

Composition.—The following fats and fatty oils, amongst others, contain oleïn, stearin, and palmitin: fat of men, sheep, oxen, geese, and pigs, of cantharides, cocoa beans, oil from seeds of species of *Bassia*, from Para nuts, from cocculus indicus, and from maize. Oleïn and palmitin occur in cotton-seed oil, in bicuhyba fat, in palm oil, in the fat of beans, peas, and lupine seeds, and in elephants' fat. Oil of rape and of mustard seeds contain glycerides of erucic and behenic acids. Earth-nut oil contains glycerides of palmitic, arachic, and hypogæic acids. Cocoa-nut oil contains glycerides of formic, acetic, butyric, hexoic, octoic, decoic, lauric, myristic, and palmitic acids. The fat from the seeds of *Anacardiaceæ* contains oleïn and stearin. Croton oil contains glycerides of formic, acetic, isobutyric, isovaleric, tiglic, palmitic, stearic, lauric, myristic, and oleïc acids. Almond oil consists almost entirely of oleïn. Nutmegs contain myristin. Castor oil contains glycerides of stearic and ricinoleïc acids. Linseed oil consists chiefly of the glyceride of linoleïc acid, but contains also those of palmitic and myristic acids. Cod liver oil consists chiefly of oleïn and palmitin, but it contains also small quantities of acetic and butyric acid and some compound of iodine. The oils from poppy seeds and from walnuts contain glyceryl linoleate and other glycerides. Butter contains glycerides of palmitic, stearic, myristic, arachic, butyric, hexoic, octoic, and decoic acids.

FATTY ACIDS *v.* ACIDS.

FATTY ALCOHOLS *v.* ALCOHOLS.

FATTY COMPOUNDS. This term is applied to all organic compounds whose molecules are supposed not to contain a closed chain of carbon atoms.

FEHLING'S SOLUTION. An alkaline soluton of potassio-tartrate of copper used in the estimation of glucose, which reduces the solution with ppn. of red Cu_2O. Fehling (*A.* 72, 106; 106, 75) dissolves 192 grams $NaK.C_4H_4O_6$ crystals in a little water, adds 600-700 c.c. NaOHAq S.G. 1·12, and then 40 grams $CuSO_4.5H_2O$ in about 160 c.c. water, and dilutes to 1154·4 c.c. at 15°. Five milligrams of dry glucose ppt. all the Cu as Cu_2O from 1 c.c. of this solution.

M. M. P. M.

FELLIC ACID $C_{23}H_{40}O_4$. [120°]. An acid said to accompany cholic acid in human bile

(Schotten, *H.* 11, 268). Strongly electrical powder, tastes bitter. It gives a red, but not a crimson, colour with Pettenkofer's test.—BaA'_2 4aq. S. 1·3.—MgA'_2 2½aq.

FENNEL OIL. The oil of common fennel (*Anethum Fœniculum*) contains anethol and a terpene (phellandrene) (c. 187°) (Cahours, *A.* 41, 75).

FERMENTATION AND PUTREFACTION. Most organic compounds exposed to the air undergo decomposition at a more or less rapid rate. The decomposition takes place most rapidly in the presence of moisture and at a slightly elevated temperature. In most cases the decomposition consists in the breaking down of complex molecules either by the assimilation of the elements of water (*hydrolysis*) or by a slow process of oxidation (*eremacausis* or *decay*). In other cases the change seems to be one of molecular rearrangement resulting in the alteration of the physical properties of the body, such as the conversion of a solid into a liquid metameride. When these changes are accompanied by the evolution of gases of unpleasant odour, the term *putrefaction* is used, and it may therefore be regarded as a special case of fermentation. The earliest experiments on these phenomena have established the facts that decomposition does not take place if air be excluded, if the materials be dry, if the temperature be below 0°C. or above 100°C., or in the presence of certain organic and inorganic bodies, which, from having the property of arresting or preventing these changes, are called anti-septics, anti-ferments or anti-putrescent substances. Formerly it was held that these changes were due entirely to the action of chemical and physical forces, but it is now known that in most cases, and possibly in all, the decomposition cannot take place without the intervention of living organisms or of chemical substances, which, although of an unorganised constitution, are derived directly from living protoplasm. The bacteria and certain fungi are the best-known organisms which determine these changes. Each bacterium characterised by its particular form and growth feeds on a particular pabulum or chemical food causing it to break up and form definite chemical products, so that there is found in each kind of fermentation the same conditions and the same kind of organism. The reasons which have led to the above view are based not only upon the conditions which are found necessary for the fermentation to take place but also upon the fact that a nitrogenous body is always found in the liquid even when the chemical change consists in the breaking down of a non-nitrogenous compound. In some cases fermentation is brought about in a manner which appears to be different from the foregoing, no organisms being present, and the addition of certain anti-ferments fail to stop the decomposition. In these cases bodies of complicated constitution, and directly derived from vegetable or animal organs, must be present. They are without organic structure, and are known as chemical or unorganised ferments or *enzymes*, and may in most cases be extracted from the organs in which they occur by means of glycerin, and can subsequently be precipitated from the solution in an amorphous condition by the addition of alcohol. The enzymes seem to be an intermediate product of organic life. None have been prepared artificially, and plant and animal organs by the secretion of these substances are enabled to perform their special functions. Their characteristic properties are destroyed when their aqueous solutions are warmed to a temperature near to 100°C., and no action takes place when the solution is cooled below another fixed temperature. These critical temperatures vary with the different enzymes, but the range of temperature approximates to 50°–75°C. Great concentration of the solution and the addition of glycerin or alcohol alter the temperatures at which the enzymes cease to act. Dry enzymes can be heated to the boiling-point of water and even higher without destroying their property of fermenting. Dried pepsin can be heated to 170° without losing its fermenting action (Hüppe, *C. C.* 1881, 745). Light also modifies the rate at which the enzymes ferment.

Theories of fermentation. From the fact that contact with air and the presence of a nitrogenous body are necessary for fermentation or putrefaction to take place, Berzelius and Liebig concluded that the nitrogenous matter was decomposed by the atmospheric oxygen, and that this reaction caused a rearrangement of its elements which determined the decomposition of the molecules of the fermentable substance present. Schwann's discovery of the presence of organic germs in the air led Pasteur to formulate the theory that fermentation is never excited except under the influence of microscopic organisms, and further that each particular organism sets up a peculiar species of fermentation. Schwann and Helmholtz showed that air which had passed through a red-hot tube could not induce fermentation, and thereby proved that oxygen alone was not sufficient to bring nitrogenous matter into the condition of a ferment. Blondeau was the first to show that the conversion of sugar into alcohol was due to the growth of one particular organism (*Torvula cerevisiæ*), and that the conversion of sugar into lactic acid was due to the growth of the mould *Penicillium glaucum*, and that beer yeast contained the germs of both these organisms. Blondeau also pointed out that in butyrous fermentation or the formation of butyric acid from sugar, and in the conversion of urea into carbonate of ammonia, a growth of *Penicillium glaucum* accompanied the change. These views of Blondeau, Pasteur, and Schwann, were contested by Liebig, who adduced experiments in support of his own view. Schmidt (*A.* 61, 168) pointed out that by adding the clear filtrate from the paste produced by beating almonds with water to a liquid containing urea or grape sugar, fermentation took place, and when the latter substance was employed, no trace of yeast cells was manifest until the fermentation had taken place for a considerable time. Pasteur (*Bl.* 1861, 67–79) produced additional evidence to show that ready-formed yeast would germinate and grow to a limited extent in a liquid containing sugar and albuminous matter, even when oxygen was completely excluded. He explained this result by assuming that the yeast acted as a ferment in the absence of air by abstracting oxygen from the sugar, and that upon this deoxidising power its action as a ferment depends. Organisms which are aerobic, and live by means of the oxygen of the air, might become anaerobic and derive their oxygen from some ready-formed compound and thus act as ferments. Pasteur also extended his researches on the action of ferments to the phenomena of putrefaction and decay, and (*C. R.* 56, 734, 1189) defined putrefaction as a kind of fermentation induced and maintained by organisms of the genus *Vibrio*, which can only live in contact with the air. He showed that when calcium lactate ferments in the absence of air, calcium butyrate and other products are the final result, whilst, if air has access to the liquid, the butyrate likewise ultimately disappears. The putrefaction of solid bodies (animal carcases) is also due to the activity of these organisms, whose development can be checked by inclosing the substance in a closed vessel containing a cloth soaked in spirit or by other antiseptic treatment. The gangrene which is subsequently produced under these conditions is regarded by Pasteur as distinct from putrefaction, and as analogous to the ripening of fruits after their separation from the plant on which they grow. These experiments of Pasteur were criticised by Lemaire (*C. R.* 57, 958), who regarded the various processes of fermentation as due to the action of one and the same ferment, and denied the existence of special ferments. He also concluded that the unrestricted access of air was essential to the progress and completion of putrefaction. Pasteur (*C. R.* 73, 1419) drew attention to the fact that properly selected mineral salts were necessary for the growth of fermentative germs. He found that the addition of small quantities of NH_4, Mg, Ca phosphates and $(NH_4)_2SO_4$ to a solution of calcium lactate increased the rate at which the lactate disappeared on the addition of vibrios, and that at the same time numerous fresh vibrios were produced. As soon as the whole of the lactate was decomposed the vibrios fell dead to the bottom of the vessel. Again (*C. R.* 75, 784) he showed that the same cells acquire or lose the power of acting as a ferment according as they are deprived of air or exposed to its action. Yeast and other ferments can therefore live and multiply without contact with the atmosphere by obtaining the oxygen necessary for their existence from the decomposition of the oxygenated compounds in which they live. The moulds, such as *Penicillium glaucum*, become ferments when they feed in this manner upon bodies rich in oxygen instead of absorbing atmospheric oxygen. Evolution of heat usually accompanies fermentation; the compounds, which are decomposed, being of a high order of complexity, evolve heat in their resolution into simpler molecules of a more stable nature. The spontaneous combustion of some organic bodies is probably due to the action of ferments. Bodies rich in nitrogen are very prone to putrefaction, but some, such as uric acid, the alkaloids and indigo, do not undergo any change. The gases evolved in fermentation may be carbonic acid, ammonia, sulphuretted hydrogen, hydrocarbons, nitrogen, and hydrogen. Bérard drew attention to the fact that fruits exposed to an inert gas evolve carbonic acid, and Pasteur showed that alcohol was at the same time produced which pointed to a sort of fermentation taking place. The earlier experiments on the action of reagents upon ferments showed that neutral gases and dilute acids do not affect the power of yeast, but that sulphur is reduced to sulphuretted hydrogen when added to a fermenting liquid. Dilute alkalis retard fermentation and large doses of dilute acids completely stop it. The behaviour of other reagents upon fermenting liquids is discussed under *antiseptics* at the end of the present article. The influence of pressure on fermentation has been studied by H. T. Brown (*C. J.* [2] 10, 570; 11, 973). According to his experiments, N, H, paraffin hydrocarbons, and NO are evolved, besides CO_2 in the alcoholic fermentation of grape sugar or malt wort. Diminution of pressure causes a large increase of the gases unabsorbed by KHO. The increase of hydrogen is accompanied by the formation of acetic acid and aldehyde, and no nitrogen is evolved from solutions free from albuminoids. The nitric oxide is due to the reduction of nitrates under diminished pressure, less sugar is decomposed, and the proportion of carbonic acid to alcohol is greater. The influence of temperature on fermentation has been studied by many observers chiefly from an industrial point of view. Pierre (*C. R.* 73, 317) showed that high temperatures in alcoholic fermentation were attended with a more abundant formation of the higher alcohols. When the temperature is kept down to the lowest point, traces only of butyl and amyl alcohols are obtained. Propyl alcohol is always produced. Contributions to the study of fermentation by Brefeld (*B.* 7, 281), Mayer (*B.* 7, 579) and Traube (*B.* 7, 872) conclusively proved that yeast requires for its growth and propagation free oxygen. Fermentation takes place in the absence of free oxygen, but in this case the yeast does not increase. Moritz (*C. J.* 1874, 599), Mohr (*B.* 7, 1421) and Pasteur (*C. R.* 80, 452) disagree with their results, and still more recently Berthelot has published the laboratory notes of C. Bernard which tend to support the observations of the former experimentalists. According to Bernard (*C. R.* 87, 125), alcoholic fermentation is not life without air, for alcohol is formed by contact of sugar with air without yeast. The ferment is not derived from external germs, for in sterile juices the ferment is not developed; alcohol is formed by a soluble ferment apart from the life of the ripening fruit for which air is absolutely necessary. The soluble ferment is found in the juice expressed from the fruit, and it produces alcohol in the expressed juice. It will be seen from the above summary that the present condition of the subject is very unsatisfactory, and that further experiments in nearly every direction are needed with pure materials and known organisms. Much of the past work has been done by chemists who have neglected the biological portion of the work, or biologists who have not noted the exact chemical changes which occur. Steps towards a better grasp of the subject are being made by several investigators. Experiments by Fitz, Marpmann, and more recently by Warington and Percy Frankland, have given definite data for future work. These experiments were made with pure cultivations of known organisms, and the amount and quality of chemical change carefully determined. Recent work seems to indicate that bacteria and moulds, living anaerobic, bring about most fermentations, and that, for these organisms to live, certain conditions are necessary, the most important of which is that their special nitrogenous pabulum is present. The way in which the enzymes or unorganised ferments act is still imperfectly understood. The decomposition effected by their agency is not so complete as in the other cases. Generally the change appears to be one of molecular rearrangement only, and no alteration in the distribution of energy takes place. Bacteria may, however, play an important part in the changes which are now attributed to these unorganised ferments, and they may, therefore, only be the means of educating some of the common bacteria into doing special work. All the unorganised ferments contain nitrogen, and it is certain that the bacteria cannot live without some nitrogenous substance being present. It is known that the same species of bacterium, by varying the conditions of life, is capable of giving very different chemical products. It may be that the unorganised ferments do not by themselves determine the change, but that bacteria are induced by them to work in special manners. When we consider the various food-stuffs which are resolved by the higher organisms into the same products, we see that the same organism is capable of a wide range of pabulum or can bring about a great number of chemical decompositions. Wortmann, on the other hand, is of opinion that bacteria effect fermentation by producing first an unorganised ferment which then brings about the changes which are ascribed to the bacteria. Yeast, for example, secretes an unorganised ferment, invertin, which has the property of resolving cane sugar into glucose. Starch is also converted into a sugar capable of reducing cupric oxide by bacteria in the absence of other sources of carbon nutriment, and this action is due to the secretion of a ferment by the bacteria. The ferment is soluble in water and precipitable by alcohol. It acts on starch in the absence of oxygen and is secreted by bacteria in a neutral starch solution. It does not possess any peptonising properties, but under different conditions the same bacteria can form (1) an amylolytic (diastatic) ferment, and (2) a peptonising ferment (Wortmann, *H.* 6, 287-329). Warington has shown that *Micrococcus gelatinosus*, *M. ureæ*, *B. fluorescens liquescens*, soil and Koch's cholera spirillum curdle milk readily without producing any appreciable acidity. The curdling cannot be due to the formation of lactic acid, but points to the secretion of a rennet-like ferment by these organisms (Warington, *C. J.* 1888, 737). Stutzer has likewise found that moulds grown in a solution of salts and tartaric acid formed albumen and nuclein (*H.* 6, 572-574). Yeast, according to Hoppe-Seyler, also forms nuclein.

Fermentation processes may for our present purpose be conveniently classified according to the principal products formed.

Ethyl alcohol is formed from sugars, starch, and glycerin. *Propyl*, *Butyl*, *Amyl*, *Hexyl*, and *Heptyl* alcohols are all produced under suitable conditions. The formation of *mannite* and *gum* from sugar, and the *ferment oils* may also be included under the heading of alcoholic fermentation.

Fermentation resulting in the production of acid bodies includes the formation of *acetic acid* from alcohol, *butyric acid* from lactic acid, *lactic acid* from sugar, and *nitric* and *nitrous acids* from ammonia. *Ammonia* from urea and the *ptomaines* from albumen are examples of basic fermentation.

The enzymes as we have seen do not form such simple products as are produced when the fermentation is the result of the action of bacteria and moulds. They may be classified into: 1. *Sugar-forming*, including diastase, ptyalin, myrosin, emulsin, invertin, and the ferment of the pancreas. 2. *Peptone-forming*, including pepsin, papain, and trypsin. 3. *Albumen-forming*, the more important of which are the ferments of the liver and blood and chymosin. 4. *Glycerine-forming* or fat-decomposing, of which the ferment of the pancreas and Fremy's pectase are examples. 5. According to Musculus an unorganised ferment exists in urine and *forms ammonia* from urea (*Pf.* 12, 214). Mayer (*Lehre von den Chem. Fermenten*, 1882, 82-91) has examined the quantity of enzyme required to produce a given amount of decomposition, and has shown that the amount of fermentation varies directly with the amount of ferment employed. He has also established the fact that the enzyme is not destroyed by its own ferment action. The precise manner in which the chemical ferments act has been the subject of much speculation. Most of the facts can be explained on a theory of action similar to that of sulphuric acid in etherification, but a 'contact' theory seems more probable. If the enzymes by their presence raise the molecular temperatures of the decomposing molecules to the point at which their molecular equilibrium is destroyed, then decomposition is produced by rearrangement of energy and not by any increase or decrease of the amount present in the system.

1. **Alcoholic or Vinous fermentation.** Solutions containing glucose $C_6H_{12}O_6$ in contact with the air at temperatures between 20°-24°C. become turbid, give off CO_2, and after some time have the whole of the sugar converted into alcohol. Glycerin, succinic acid, and the higher alcohols are at the same time produced. When the evolution of carbonic acid ceases the ferment or yeast (*Torula* or *Saccharomyces cerevisiæ*) separates leaving the liquid clear. The separated yeast is capable of inducing fresh fermentation in further quantities of sugar solution. Cane-sugar and milk-sugar also undergo various fermentations, but they are first hydrolysed by the ferment or commercially in other ways. Other ferments induce the vinous fermentation of sugar, *e.g. erythrozym* the madder ferment (Schunck, *J. pr.* 63, 222) besides fungi. Reess (*Bot. Untersuch. ü. d. Alcoholgährungspilze*) gives the following list of fungi which incite alcoholic fermentation :—*Saccharomyces cerevisiæ*, *S. ellipsoideus*, *S. pastorianus*, *S. apiculatus*, *S. exiguus*, *S. albicans*, *Mycoderma* (rarely), *Mucor racemosus*, *M. circinelloides*, *M. spinosus*, *M. stolonifer*, *Exoascus alnitorquus* (Sadebeck), *Torula* and *Eurotium aspergillus glaucus*.

The following fungi do not form alcohol when sown in sugar solutions :—*Saccharomyces glutinis*, *Mycoderma* (generally), *Exoascus pruni*, *Dematium pullulans* and *Fumago*. The nomenclature of the fungi is continually being modified, and Hansen of Copenhagen has restricted the genus *Saccharomyces* to the three species, *cerevisiæ*, *ellipsoideus*, and *pastorianus*, as they are the only sprouting fungi which form ascospores. Chemically yeast consists of cellulose (35), protein (45), peptone (2), fat (5), ash (7), and extractive matter (4) (Nägeli and Low), and the various yeasts have approximately the same composition. Schützenberger (*C. R.* 78, 493) has found that yeast when boiled with water yields an extract containing phosphates, gum arabin, leucine, tyrosine, carnine, xanthine, guanine, hypoxanthine, sarcine, and a sweetish uncrystallisable syrup still containing nitrogen. According to Béchamp fresh yeast contains neither tyrosine nor leucine (*C. R.* 78, 645). Rey-Pailhade (*C. R.* 107, 43) has shown that an organic compound named philothion, having the property of hydrolysing sulphur in cold solutions, is formed in the life processes of yeast. Concentrated methyl alcohol readily extracts it from the yeast. Dumas had previously noticed the property which yeast has, of forming SH_2 from S. Pure yeast is best prepared by allowing fermentation to take place in a sugar solution in which a quantity of alcohol varying from 5–8 p.c. has been added, and the temperature not allowed to exceed 15°C. Such yeast can be grown in a solution rich in albumen at about 30°C. without any bacteria appearing (Traube, *B.* 9, 183, 1239). Hansen has devised a commercial method for obtaining pure yeast (Salomon, *J. Soc. Arts*, 1888). (For the composition of yeast *v.* Belohoubeck, *J.* 1875, 898; Schützenberger a. Destrem, *C. R.* 88, 287, 383; Rommier, *C. R.* 98, 1594.) Vinous fermentation only takes place in dilute solutions of sugar, and as an increase of yeast takes place in fermentation, the liquid in addition to sugar must contain the elements necessary to form cellulose and protoplasm (P, K, Mg, Ca, and S) and a nitrogenous food. Proteids or peptones are the best form for the nitrogen, but acetamide, methylamine, ethylamine, propylamine, asparagine, and leucine, are all assimilated by the yeast cells (Nägeli). Oxamide and urea supply nitrogen but not carbon, while cyanogen compounds yield up their carbon but not the nitrogen to these organisms. Formic and oxalic acids are also unsuitable for the carbon supply of these fungi. Yeast loses a considerable portion of its fermenting power by pressure, and still more by washing with water.

Glycerin also deprives yeast of its fermenting power (Gunning, *B.* 5, 821). The influence of the age of the yeast on fermentation has been studied by Regnard (*C. R. Soc. Biol.* [8] 4, 442). Maltose and glucose are the two sugars which are most readily fermentable by yeast. All the true Saccharomyces ferment maltose, but *S. exiguus* and *S. apiculatus* are unable to decompose this sugar. The more complex carbohydrates are sometimes hydrolysed or inverted before alcoholic fermentation takes place. The higher dextrins are hydrolysed into malto-dextrin and subsequently split up into maltose and dextrin by *S. pastorianus* and *S. ellipsoideus*. *S. cerevisiæ* is unable to resolve malto-dextrin into maltose and dextrin. The conversion of cane-sugar into glucose is apparently brought about by a soluble ferment termed invertin, which is secreted within the cells of all true saccharomyces (Donath, *B.* 8, 795). This soluble ferment has been isolated in the form of a powder. It is not formed by *S. apiculatus* nor by four out of the five varieties of Pasteur's *Torula* (Hansen). *Monilia candida* ferments cane-sugar, but there is no invertin formed, the inversion being probably due to the secretion of some other soluble ferment. *Mucor racemosus* and *M. mucedo* both set up alcoholic fermentation in solutions of glucose. *M. racemosus* does not ferment inulin, but readily ferments the levulose prepared from it. The alcoholic fermentation due to *M. mucedo* takes place in the absence of oxygen at temperatures between 25°–28° C. Succinic acid but no glycerin is produced by this fungus (Fitz, *B.* 6, 48). Dextrin, inulin, and milk-sugar do not ferment under the influence of mucor.

The alcoholic fermentation of milk-sugar according to Blondlot is brought about by a special alcoholic ferment which does not manifest any action below 20°, and then only when the liquid is agitated. A small quantity of butyl alcohol is at the same time produced. Vieth has also shown that yeast does not readily set up alcoholic fermentation in solutions of milk-sugar. Kefir grains, which contain a bacillus termed *Diospora caucasiæ* by Kern and a modified form of *S. cerevisiæ*, produce a rapid alcoholic and lactic fermentation in milk-sugar solutions (*Analyst*, 12, 2).

Ethyl alcohol is obtained from other substances by fermentation.

According to Fitz (*B.* 9, 1848; 10, 276; 11, 42) alcohol is produced when schizomycetes are added to a solution of glycerin, mannite, starch, dextrin, milk-sugar, or dulcite, but, as the fermentation only takes place in the presence of some nitrogenous material, pepsin or ammonium sulphate is added to the solution. Acids are at the same time produced, *n*-butyric acid being the one most frequently formed. Quercite yields no alcohol and only *n*-butyric acid.

The quantities of the products formed in alcoholic fermentation vary with many conditions which have not yet been fully determined. Glycerin, succinic acid, and traces of high alcohols are almost always produced. An analysis of the products obtained by the fermentation of 100 kilos. of sugar by *S. ellipsoideus* gives the following numbers in grams:

Ethyl alcohol 50615·0, *n*-propyl alcohol 2·0, isobutyl alcohol 1·5, amyl alcohol 51·0, ethyl heptoate 158·0, glycerin 2120·0, acetic acid 205·3, succinic acid 452·0, and traces of aldehyde. Small quantities of bases appear likewise to be produced, and *n*-butyl alcohol and butyric acid are frequently formed. An examination of the products of the fermentation of sugar solutions by different yeasts has been made by Claudon a. Morin (*Bl.* 49, 178–189). Lindet (*C. R.* 107, 182) has shown by experimenting with the same yeast on the same wort that the amount of higher alcohols produced varies with the temperature. The maximum amount of ethyl alcohol is produced at the same temperature (8°–10°C.) as that when the amount of higher alcohols is a minimum (·52 p.c.). At the temperature 25°–27°C. ·59 p.c. of the higher alcohols was produced.

Formation of the higher alcohols by fermentation.—Fitz (*B.* 13, 36, 1311) has shown that the schizomycetes form *n-propyl alcohol* from glycerin. It is also a constituent of most fusel oils.

n-Butyl alcohol has been obtained by the same observer by the action of a bacillus allied to, but somewhat larger than *B. subtilis*, on glycerin in the presence of CaCO$_3$ (*B.* 11, 42, 1892; 9, 1348). Vigna (*B.* 16, 1438) has suggested this formation of *n*-butyl alcohol as a method of its preparation, since the yield is 9 p.c. of the glycerin used.

Iso-butyl alcohol has been found in the fusel oil from mangolds (Wurtz, *A. Ch.* [3] 42, 129).

Isoamyl alcohol is the principal constituent of the fusel oil formed in the ordinary fermentation of potatoes. Pierre (*J.* 1871, 832) has shown that the higher the temperature of fermentation the greater the quantity of this alcohol. An active and an inactive amyl alcohol have been separated from fusel oil. Iso-butyl and traces of other alcohols are also formed (Perrot, *A.* 105, 64). In Swedish fusel oil Rabuteau has found *propyl, iso-propyl, iso-butyl, iso-amyl alcohols, methyl propyl carbinol* and liquids boiling above 132° (*Bl.* 33, 178) (*v.* Wyschnegradsky, *A.* 190, 365).

n-Hexyl and *n-heptyl alcohols* also occur in fusel oils (Faget, *A.* 88, 325; *J.* 1862, 412).

Lebel has shown that *Penicillium glaucum* acts upon the methyl-propyl-carbinol obtained by the reduction of methyl propyl ketone, yielding an alcohol which has a lævorotation of −12° (Lebel, *J.* 1879, 492).

Mannite and gum, under certain conditions, are formed from cane-sugar. Pasteur (*Bl.* 1861, 30) pointed out that when this *mucous fermentation* takes place in solutions of cane-sugar, CO$_2$, mannite, and a mucilaginous substance are produced. Access of air and nitrogenous matter are necessary for this fermentation. Neither acid nor alcohol is produced, and the fermentation only takes place in neutral or slightly alkaline solutions (Bauer, *B. C.* 1882, 630). This kind of fermentation has been noticed in solutions of cane-sugar, beet juice, carrot juice, the juice of mangold wurzel, and in lemonade. Baudrimont (*C. R.* 80, 1253) observed the occurrence of a spontaneous viscous fermentation in a solution of crystallised cane-sugar (*v.* Hochstetter, *J. pr.* 29, 30; Kircher, *A. Ch.* 31, 337; Plagne, *J. Ph.* 26, 248; Commaille, *M. Sci.* 3, 435, 673, 772).

A white substance resembling *cellulose* is formed under certain conditions in beet juice and beet molasses. It is precipitated from the solution by the addition of alcohol. Certain fatty seeds (rape, colza, &c.) form cellulose from saccharose (Durin, *C. R.* 82, 1078; Pasteur, *C. R.* 83, 176). For the fermentation of cellulose itself *v.* Tappeiner, *Z. B.* 24, 105; Hoppe-Seyler, *B.* 16, 122; Popoff, *Pf.* 10, 113.

Lecuartier and Bellamy have shown that certain fruits and roots under the influence of oxygen become the seat of an alcoholic fermentation characterised by the evolution of carbonic acid and the disappearance of sugar in the tissues of the plant cells. From these and other experiments Pasteur considered that if plants could continue to live in an atmosphere of carbonic acid they would become ferments for sugar. Muntz (*C. R.* 86, 49), on examining this intracellular alcoholic fermentation of plants, has arrived at the following results:—1. That plants preserved in air give no trace of alcohol. 2. That plants placed in an atmosphere of nitrogen form appreciable quantities of alcohol, sometimes amounting to 1,000 times the total weight of the plants. 3. That the plants when returned to the air remained perfectly healthy. The living cell, then, in the higher plants is capable, in the absence of oxygen, of acting like the cells of fungi in producing a true alcoholic fermentation. The volatile oils, which are produced by the fermentation of various plants, may owe their origin to some such similar action of the living cells of the plant in the absence of oxygen. They are known as FERMENT OILS, and are formed when portions of the plant are left to ferment in water, and can then be distilled from the liquid. The distillate is then saturated with common salt and extracted with ether. Little is known as to the constitution of these bodies. Berzelius regarded them as peculiar alcohols related to fusel oil (*B. J.* 27, 541). They have been examined by Bley, Landerer, Büchner, and others. The following is a list of the more important plants from which ferment oils have been obtained:—*Chærophyllum sylvestre, Chelidonium majus, Conium maculatum, Erythræa centaurium, Echium vulgare, Erica vulgaris, Marrubium vulgare, Achillea Millefolium*, various species of *Plantago, Quercus robur, Salix pentandra, Salvia pratensis, Trifolium fibrinum, Tussilago farfara, Urtica urens*, and *Vitis vinifera.* A similar ferment oil is produced in cellulostasis, a disease of the apple (*Gm.* 14, 413).

On alcoholic fermentation the reader may consult for further information—Amthor, *H.* 12, 64; Béchamp, *C. R.* 88, 719; Berthelot, *C. R.* 89, 806; Cochin, *C. R.* 89, 786; 89, 992; Giacosa, *B.* 12, 703; Hoppe-Seyler, *B.* 12, 702; Petit, *C. R.* 73, 267; Schützenberger, *C. C.* 1877, 73; Schützenberger a. Destrem, *C. R.* 88, 593.

The formation of acids by fermentation. The conversion of alcohol into acetic acid seems to be a catalytic action, as platinum black and other finely-divided substances facilitate the transfer of the atmospheric oxygen besides the organisms which bring about the same change.

Acetous fermentation takes place in presence of a fungus *Mycoderma aceti*, vinegar plant or mother of vinegar, and a bacterium (*B. aceti*). Both these organisms are usually present, and apparently the bacterium completes the work of the mycoderma. It is believed that the function of mycoderma is to convert starch into alcohol, and that the alcohol produced in this or other ways forms the pabulum of the *B. aceti*, which causes the oxidation of the alcohol to acetic acid. K, Mg, NH$_4$, and H$_3$PO$_4$ are necessary for the growth of mycoderma (Pasteur, *J.* 1861, 726; 1862, 475). The same organisms appear to be capable of completely oxidising the acetic acid which they form to carbonic acid and water, if it be not removed. This is especially the case if the growth be allowed to sink to the bottom of the liquid. A temperature ranging from 20°–35° is the best for the change, and above 50° all fermentation ceases.

The formation of acetic acid at times accompanies alcoholic fermentation (Béchamp, *J.* 1863, 773; Blondeau, *C. R.* 57, 953; Pasteur, *Études sur la vinaigre*, Paris, 1868). Acetic acid is also produced, together with butyric acid, in the fermentation of a mixture of malt, milk, chalk, and rancid meat (Grillone). According to Béchamp (*C. R.* 76, 836) it is normally present in milk, together with alcohol, as a product of the action of microzymes.

Acetic acid and butyric acid are formed by the action of yeast, at a temperature of 20°–30°, on citric acid, to which excess of chalk has been added. Putrefying curd and a base effect the same change (How).

Lactous fermentation or the formation of *lactic acid* from the sugars—glucose, cane- and milk-sugar—takes place when these bodies are mixed with fresh sour cheese, or with milk and chalk. After some time the lactic acid is itself attacked, and H, CO_2, and butyric acid are produced. The lactic fermentation only takes place in a neutral or slightly alkaline solution. This condition is obtained by adding chalk or zinc white to the sugar solution. Traces of mannite are also formed (Fremy, *A.* 31, 188; Boutron, *A.* 39, 181; Bensch, *A.* 61, 174; Lautermann, *A.* 113, 242). The decomposition of the calcium lactate into butyric acid appears to be due to the action of a bacillus (Pasteur, *J.* 1862, 477). The schizomycetes resolve it into *propionic acid* (Fitz, *B.* 11, 1898; 12, 479; Strecker, *A.* 92, 80), acetic acid, and sometimes *n-valerianic acid* (Fitz, *B.* 13, 1309). The fermentation of calcium lactate by the butyric ferment of Pasteur yields butyric acid, propionic acid, *n*-valerianic acid, and some ethyl alcohol (Fitz, *B.* 13, 1310). The ordinary lactous ferment, according to Pasteur (*A. Ch.* [3] 52, 404), is *Penicillium glaucum.* It resembles beer yeast, and is grey in colour, and has been described by Pasteur and Blondeau. Free acid retards its action, nitrogenous matter favours it, desiccation or boiling with water weakens it. All the sugar can be converted into lactic acid if ammonium salts and phosphates be present. Lactous fermentation often accompanies vinous fermentation (Blondeau, *J. Ph.* [3] 12, 257). The change may be brought about by the presence of a special bacterium (*B. acidi lactici*) which accompanies the growth of *P. glaucum.* The conditions of lactic fermentation have been examined by Richet (*C. R.* 88, 750; *C. J.* 36, 663) and Berthelot (*A. Ch.* [3] 55, 351).

Butyric fermentation.—We have seen that butyric acid is the final product in the lactous fermentation of sugar solutions. The conversion of lactic into butyric acid is accompanied by the evolution of hydrogen and carbonic acid, and butyl alcohol is also produced. The ferment, according to Pasteur, is a bacillus (*C. R.* 52, 344), which requires no oxygen for its life, and is not killed when carbonic acid is passed into the liquid. Ammonia and phosphates are necessary for the development of this fermentation (Pasteur, *Bl.* 1862, 52). Béchamp attributes the change to a ferment existing in the chalk which is added (*Bl.* [2] 6, 484), and Baudrimont to an unorganised ferment (*C. R.* 80, 1253). Boehm (*B.* 8, 634) has observed that butyric fermentation accompanies the evolution of marsh-gas and ammonia, when plants are immersed in water free from air. Twigs of *Elodea canadensis* immersed in sugar syrup set up a fermentation which gives butyric acid, butyric ether, carbonic acid, and hydrogen (Schützenberger, *C. R.* 80, 328, 497). According to Fitz (*B.* 9, 1348), glycerin saturated with calcium carbonate undergoes fermentation, yielding butyric acid, *n*-butyl alcohol, and traces of ethyl alcohol. Fibrin also forms ammonium butyrate by fermentation (Wurtz, *A.* 52, 291), and Fitz has found that pepsin and glycerin, in presence of chalk, is fermented by schizomycetes at 40° into *n*-butyl alcohol, *n*-butyric acid, besides traces of ethyl alcohol and a higher acid, probably *hexoic* (*B.* 9, 1348; 10, 276; 11, 42). Pribram (*J.* 1879, 614) has formed butyric acid by the action of the ferment of calves' liver on starch paste, and Fitz has found that *B. subtilis* ferments potato-starch containing salts into butyric acid and small quantities of alcohol, acetic and *succinic* acids (*B.* 11, 52). Other contributions to our knowledge of this kind of fermentation are by Iljenko a. Laskowsky, *A.* 55, 85; Iljenko, *A.* 63, 268; Grillone, *A.* 165, 127.

Gluconic acid is produced by the fermentation of glucose solutions by *Mycoderma aceti* (Boutroux, *C. R.* 91, 230). Maumené contends that this change is merely oxidation, as copper acetate and mercuric oxide give similar results (*C. R.* 91, 331).

Nitrification. The term given to the oxidation of ammonia to *nitric and nitrous acids* by an organism or organisms present in the soil. The formation of nitre in nature, and artificially in nitre beds, is due to the same cause. Many experiments have conclusively proved that the direct combination of oxygen and nitrogen does not take place to any large extent in nature, and even ozone appears to be incapable of oxidising nitrogen. Kuhlmann was the first to explain the presence of nitric acid and nitrates in the soil as due to the oxidation of ammonia. This theory is now held, but the oxidation is indirectly brought about by the action of organisms. The first suggestion that the oxidation of ammonia and organic nitrogen in the soil is the work of a living organism was made by Pasteur in 1862. Müller, in 1873, showed that the ammonia of sewage and of impure well waters changed spontaneously into nitric acid, whereas solutions of pure ammonium salts and urea remained unchanged. Schlœsing and Müntz (*C. R.* 77, 203, 353; 84, 301; 85, 1018; 86, 982; 89, 1074) have established this hypothesis by experiment, and Warington (*C. J.* 33, 44; 35, 429; 45, 653; 51, 118), at Rothamsted, has shown that the nitrification in soil and in waters is due to an organised ferment. The organism is destroyed at 100°C., and by $CHCl_3$, CS_2, and phenol. *Penicillium glaucum*, *Aspergillus niger*, *Mucor mucedo*, *M. racemosus*, *Mycoderma vini* and *M. aceti*, as well as the ordinary forms of bacteria present in the atmosphere, are all incapable of effecting nitrification. Schlœsing and Müntz state that they have isolated the organism in minute round or slightly elongated corpuscles, which multiply by budding, and appears to be a micrococcus. The fermentation takes place in presence of alkaline carbonates or calcium carbonate. Besides the humic matter of soil, tartaric acid, sugar, alcohol, glycerin, and albumen are effective as food for the growth of this organism. Light is not favourable to nitrification. The change commences slowly, gradually attains a maximum of energy, and then becomes slow again. The formation of nitrous acid by this organism is rare in the soil, but frequent in liquids. The influence of temperature, concentration of the solution, depth of liquid, proportion of organic carbon, and degree of aeration has been studied by Warington and the French observers. Warington (*C. J.* 1888, 727-755) has tested for nitrates in cultivations of upwards of twenty organisms with negative results. Heræus (*Zeit. f. Hygiene*, 1886, 193) has, however, succeeded in isolating two or three organisms which he states induce the formation of nitrite in urine and in mineral solutions containing ammonium salts. Percy Frankland has not succeeded in isolating the organism; Leone, on the other hand (*Atti d. R. Accademia d. Lincei*, 1887, 37), concludes from his experiments that all micro-organisms are more or less capable of producing nitric acid, and that the same organisms in the presence of organic matter are capable of reducing nitrates. Celli a. Zuco (*Gazz.* 17, 99), Frank (*Forsch. a. d. Gebiete d. Agriculturphysik*, 10, 56) and Adametz (*l. c.* 1886, 381) may also be consulted for further information on this subject.

Bases produced by Fermentation.

1. *Ammonia from Urea.*—The ammoniacal fermentation of urea which takes place in urinals is due to the action of a bacterium (*B. ureæ*). The urea is converted into ammonium carbonate, but the change only takes place when mucus or other organic substances are present, as urea dissolved in pure water remains unaltered. In presence of yeast the change takes place very quickly (Schmidt, *A.* 61, 168). According to Musculus (*B.* 9, 357) an enzyme is present in the urine of persons affected with catarrh of the bladder, which also brings about this change. It is precipitated by alcohol as a coagulum resembling fibrin, and decomposes urea completely into carbonic acid and ammonia at 35°-40°. It has also the power of decomposing hippuric and uric acids, creatine and guanidine. Its action ceases in the presence of dilute HCl and most other acids, but small quantities of phenol have no retarding action. Dilute alkalis and sodium chloride have no influence. More recently the presence of ferments in normal urine has been confirmed by Städelmann (*Z. B.* 24, 226, 260). He finds that pepsin is always present in normal urine, but in no instance has trypsin been discovered. This conclusion agrees with that arrived at by Leo and Hoffmann (*Fr.* 27, 123), and is contrary to the experiments of Grützner and his pupils Sahli, Gehrig, and Holovtschiner. Raw fibrin does disintegrate in alkaline urine, even in the presence of thymol, owing, no doubt, to bacteria in the fibrin; but in no instance did digestion or disintegration take place when boiled fibrin was used.

Warington has tested the ability of over twenty organisms to hydrolyse urea. A sterilised 25 p.c. solution of urine was employed. *Micrococcus* (*B.*) *ureæ* gave a considerable increase of alkalinity, and *B. fluorescens non-liquescens* a somewhat smaller increase. Arable soil gave a much larger increase than either. The other organisms used had no effect ('The Chemical Actions of Some Micro-organisms,' Warington, *C. J.* 1888, 727-755).

2. *Ammonia from Nitrates and Nitrites. Partial reduction of Nitrates.*—Meusel (*A.* [5] 7, 287) observed that water containing nitric acid and carbohydrates, and originally free from nitrites and ammonia, contained the latter after being subjected to the action of bacteria; and that water, freshly distilled and mixed with sugar, was not found to reduce nitrates when the air was excluded from it. Percy F. Frankland has recently shown (*C. J.* 53, 373) that out of thirty-two different micro-organisms examined sixteen or seventeen have the power of reducing nitrates to nitrites more or less completely. The absence of air has no influence on the result. In many cases the change is a quantitative one. Ammonia was also sometimes formed; but it was due to the decomposition of the peptone, which was the only other nitrogenous ingredient present. *B. ramosus* and *B. pestifer* have very marked nitrate to nitrite reducing action. The yield of nitrite was augmented by increasing the amount of sugar and peptone present. *B. aquatilis* does not reduce nitrate to nitrite, but causes the disappearance of nitric nitrogen, the deficiency not being accounted for by the small quantity of ammonia which was generated in the solution. According to Warington, the organisms which appear to possess the greatest power of reducing nitrates to nitrites are *B. floccus*, *B. fluorescens non-liquescens*, B. of swine fever, *M. ureæ*, *M. gelatinosus*, *Staph. candidus*, and *Staph. luteus*. The following also reduce nitrates freely: *B. termo*, B. of typhoid fever, B. of infantile diarrhœa, B. of cholera, B. of septicæmia, *B. anthracis*, B. Demcke's comma, and *Staph. albus liquescens*, *B. subtilis* yields no nitrite in a urine solution, but forms a trace of nitrite in broth after some time. *Streptococcus scarlatinæ* yields a mere trace of nitrite in broth cultures. *B. fluorescens liquescens*, *B. toruliformis*, *B. sulphureus*, B. Finkler's comma, *B. comma noma* and *M. aureus*, failed entirely to effect reduction to nitrites (Warington, *C. J.* 1888, 727-755).

3. *Bases formed in fermentation.*—Poisonous bases having properties resembling the alkaloids are produced in putrid fermentation, and also in small quantities in alcoholic fermentation. The bases formed in the putrefaction of meat and fish are known as ptomaines, and a considerable amount of literature on their formation and properties now exists, which it is impossible to deal with in the present article. Gautier a. Etard (*C. R.* 94, 1598) have shown that the complex phenomena of putrid fermentation may be regarded as brought about by the hydration of the complex albuminoid molecules into simpler molecules. Two compounds are apparently first formed, one of which is stable and gives rise to the glauco-proteins and leucines, to which Schützenberger attributes the formula $C_nH_{2n-1}N_2O_2$, whilst the other is unstable, and decomposes rapidly into NH_3, CO_2, formic, acetic, and oxalic acids.

In Schützenberger's method of hydration with barium hydrate, the amides are not hydrated, but bacteria in putrefaction slowly change them into ammoniacal salts. The crystalline body $C_{11}H_{26}N_2O_6$ produced abundantly in the putrefaction of fish also undergoes hydration when similarly treated. Putrefaction being essentially a process of hydration it follows that the aromatic derivatives and the bases produced during fermentation pre-exist as nuclei in the flesh. The bases formed in the putrefaction of the skate can be obtained by acidulating the liquid products with sulphuric acid. On evaporation, *in vacuo*, indole, phenol, and other volatile products are removed and the residue, after treatment with baryta, is extracted with chloroform. The bases are colourless oily liquids and resemble those described by Selmi. They have an odour like that of the carbylamines and hydrocollidine. By fractionation two bases, $C_9H_{13}N$ and $C_8H_{13}N$, have been isolated. The latter (110°) closely resembles Cahours's and Etard's hydrocollidine, with which it is probably isomeric. Two bases having the formula $C_5H_{11}NO_2$ and $C_7H_{15}NO_2$ have similarly been obtained from the products of the putrefaction of flesh and fibrin (Salkowski, *B.* 12, 648; 16, 1191). Brieger (*B.* 16, 1186) has extracted from putrefied horseflesh the bases $C_5H_{14}N_2$ and $C_5H_{11}N$. A base having the formula $C_7H_{10}N_2$ (171°) and soluble in most solvents has been isolated by Morin from the products of alcoholic fermentation. It forms a double Pt salt and gives precipitates with the usual alkaloid reagents (*C. R.* 106, 360). Its toxic effects have been studied by R. Wurtz (*C. R.* 106, 363). Tanret considers this base identical with (β)-glucosine obtained from glucose and ammonia (*C. R.* 106, 418). An examination of the amount of nitrogen bases present in fermented liquids (brandy, rum, &c.), has also been made by Lindet (*C. R.* 106, 280).

Sugar-forming ferments.—The more important chemical ferments which belong to this group are diastase, ptyalin, myrosin, emulsin, invertin, animal invertin, and one of the ferments which exist in the pancreas. They are found in the animal and vegetable kingdoms, in the former they are secreted by some of the principal organs, in the latter they occur in various parts of the plant. The sugar produced may be either dextrose or maltose, and the substance decomposed differs with the different ferments, starch, cane-sugar, and the various glucosides being the more important; we have already seen that the enzymes may be isolated by precipitating the aqueous extracts of the organs containing them with alcohol. They are also mostly soluble in glycerin, which may be used to extract them from the finely divided material. The glycerin extract is then dropped slowly into strong alcohol, and the precipitated ferment collected. The chemical composition of these bodies has been investigated by Krauch, Dubrunfaut, Hüfner, Donath, Barth, and others, and from their analyses it is known that they all contain a considerable percentage of nitrogen. Invertin, emulsin, and the diastatic pancreas ferment also contain sulphur. The influence of temperature and light upon their action has already been alluded to. Dried diastase can be heated to 158°, and the pancreatic ferment to 162°, without destroying their fermentative property. The amount of work which they are able to perform in a given time is, however, diminished by heating above 100° (F. Hüppe, *C. C.* 1881, 745). Chloroform, carbon bisulphide, ether, prussic acid, do not retard the action of these ferments, but most acids and alkalis hinder their action. All salts and bodies which coagulate albumen have the property of stopping this kind of fermentation. The chemical change brought about by the sugar-forming enzymes is one of hydrolysis. Diastase, ptyalin, and the diastatic pancreas ferment convert starch or glycogen into a sugar (maltose) and dextrin. The pancreatic ferment and ptyalin yield a dextrin (achroodextrin) which differs from the dextrin obtained by means of diastase in not reacting with iodine (Naffe, *Pf.* 14, 473). Invertin converts cane-sugar by hydrolysis into dextrose and levulose. The ferment action of emulsin consists in the hydrolysis of the glucosides. Glucose is the constant product of the action. The following are those decompositions which are best established. Salicin to saligenin, helicin to salicylic aldehyde, arbutin to hydroquinone and methylhydroquinone, amygdalin to benzoic aldehyde and prussic acid, coniferin to coniferyl alcohol and daphnin and convolvulin are similarly hydrolysed by emulsin. Nencki is of opinion that in hydrolysis the water is split into hydrogen and hydroxyl by emulsin (*J. pr.* 17, 103). Myrosin appears to determine the breaking up of the molecule of potassium myronate or of the free myronic acid into mustard oil, sugar, and sulphate without the assimilation of the elements of water. It seems probable that with further investigation the formula of myronic acid may be modified and that this ferment change will also be found to be one of hydrolysis (Will a. Körner, *A.* 125, 263; Franchimont's *Kort Leerboek*).

Peptone-forming ferments. Digestion.—The peptone-producing ferments, pepsin, trypsin, pepsin (of plants), and papain, convert albumen into peptone. This change apparently is brought about in a similar manner to those of the last-mentioned group, the elements of water being taken up by the albuminoid substances. Other bodies besides peptone are produced, trypsin and papain yielding crystalline amido- compounds (leucine). Wurtz is of opinion that papain acts by combining first with the fibrin, and that an insoluble product is thereby produced, which by the action of water is reconverted into the ferment and soluble substances resulting from the hydration of the fibrin (Wurtz, *C. R.* 91, 787; 93, 1104). Pepsin also seems to first form an insoluble compound with fibrin, which is subsequently broken up by water. Certain bacteria resemble these enzymes in their action, and probably have this property from secreting a similar ferment. The principal albumen-forming ferments are the liver ferment, the blood ferment, and chymosin. Ferments analogous to the liver ferment exist in the vegetable kingdom. The conversion of casein into cheese by rennet is an example of this class of fermentation, and from the analyses of these two bodies it seems probable that in this case also the change is one of hydrolysis. A ferment similar to that existing in the liver is found in certain plants, notably in *Oxalis Acetosella*, *O. stricta*, *Cirsium arvense*, *Rumex Patientia*, in the leaves of artichokes, and in the seeds of black pepper and *Wilhamia coagulans*. Certain bacteria separate a ferment which behaves like chymosin.

A ferment also exists in the pancreas, which is capable of decomposing the fats into glycerin. Not only are the triglycerides attacked, but complex molecules like lecithin are also hydrolysed.

Antiferments or Antiseptics.—Many inorganic and organic substances have the property of arresting or hindering fermentation. They act by killing the organisms which bring about the fermentation, and most of the substances which have poisonous properties have also antiseptic properties. In the earlier experiments it was noticed that while creosote and phenol arrested the development of fungi and germs fermentation still proceeded, and Buchholz (*J.* 1867, 742) found that milk turned sour when phenol was present. Naunyn (*J.* 1865, 606) noted that benzene interfered with the action of yeast on sugar solutions. Pienkowsky (*J.* 1865, 606) examined the antiseptic action of a considerable number of salts on meat with the following results:—

No antiseptic action:

Alum, $Al_2 3SO_4$, Na_2HPO_4, $Sr2NO_3$, $Ba2NO_3$, $(NH_4)_2C_2O_4$, $Na_2C_2O_4$, $BaCl_2$, Na_2SO_3, $Na_2S_2O_3$, NH_4NO_3, $KClO_3$, Na_2SO_4, K_2SO_4, $MgSO_4$, $(NH_4)_2SO_4$, $Mn(AcO)_2$, and As_2O_3.

Delayed putrefaction for one month:

KAcO, NaAcO, $Ca(AcO)_2$, NaCl, NH_4Cl, $SnCl_4$, $MnCl_2$, $ZnCl_2$, $ZnSO_4$, $FeSO_4$, K_2SO_3, and $Pb2NO_3$.

Delayed putrefaction for more than six months:

NH_4AcO, $Ba(AcO)_2$, $CaCl_2$, $CuCl_2$, $HgCl_2$, $CuSO_4$, $Pb(AcO)_2$, $K_2Cr_2O_7$, aniline nitrate, phenol, and acetic acid.

Formic acid, according to the same investigator, is a powerful antiseptic for sugar solutions. Severi (*Z.* [2] 4, 285) has examined the antiseptic action of the animal secretions. Alcoholic fermentation and putrefaction are arrested by gastric juice, but not by pepsin. Lactous fermentation is not retarded by either reagent.

Boric acid and most of its compounds have antiseptic properties. Dumas found that borax prevents the action of yeast water on sugar, of synaptose on amygdalin, and of myrosin or myronic acid. Calcium borate and boric acid either alone or mixed with glycerin prevent the formation of mildew and the putrefaction of meat. Mercuric oxide appears to be the most powerful of all antiseptics, and next to it mercuric chloride.

Among organic bodies phenol, chloral hydrate, chloroform, salicylic acid, benzoic acid, hydrocyanic acid, and thymol, all have marked antiseptic properties.

Of the alkaloids, quinine prevents, while nicotine accelerates fermentation. Calvert (*Pr.* 20, 191) found that on the addition of one thousandth part of the following antiseptics to a solution of albumen he obtained the following results:—

1. Phenol and cresol prevented the growth of fungi and bacteria.

2. $ZnCl_2$, $HgCl_2$, and zinc phenol sulphonate prevented the development of vibrios, but did not stop the production of fungi.

3. CaO, quinine sulphate, pepper, and HCN, permitted the growth of vibrios, but allowed the fungi to develop.

4. Those which had no preventive action (under these conditions). SO_2, H_2SO_4, HNO_3, As_2O_3, AcOH, KHO, NaHO, NH_3, Cl, NaCl, $CaCl_2$, $AlCl_3$, Ca(OCl)Cl, $KClO_3$, $CaSO_4$, $FeSO_4$, $CaSO_4$, $Na_2S_2O_3$, Na_2HPO_4, $Ca_3 2PO_4$, $KMnO_4$, K and Na. Phenol sulphonates, picric acid, turpentine, and wood charcoal. Sodium silicate (Rabuteau a. Papillon, *C. R.* 75, 755) prevents the alcoholic fermentation of grape-sugar, and the fluosilicates have also considerable antiseptic properties.

Salts of bismuth even in small quantities completely prevent secondary fermentations in worts (Gayon a. Dupetit, *C. R.* 103, 883–885). The influence of calomel on fermentation and the life of micro-organisms has been carefully studied by Wassilieff (*H.* 6, 112–134). The comparative antiseptic properties of $HgCy_2$, mercury oxycyanide, and $HgCl_2$, have been determined by Chibret (*C. R.* 107, 119). Ratimoff (*J. Ph.* [5] 11, 83–90) has determined the limits between which lie the minimum quantities of various antiseptics required to kill and to prevent the development of microbes and bacteria in certain media.

The relation of antiseptic power to chemical constitution has been investigated by J. R. Duggan (*Am.* 7, 62–64) by noting the amount of substance required to prevent fermentation by *bacillus subtilis* in a solution of beef peptones. The following numbers show the relative antiseptic values of the materials used: Salicylic acid, 4; *m*-oxy-benzoic acid, 6; *p*-oxy-benzoic acid, 8; phenol, 20; pyro-catech, 20; resorcin (25); hydroquinone, 30; pyrogallol, 15; methyl alcohol, 300; ethyl alcohol, 500; normal propyl alcohol, 200. Of the three phenol sulphonic acids the ortho-acid only has antiseptic and disinfecting properties in a marked degree (Vigier, *J. Ph.* [5] 11, 145–152, 214–217). Phloroglucin is possessed of no antiseptic properties, whereas pyrogallol is poisonous, and resorcin coagulates both vegetable and animal albumen (Andeer, *C. C.* 1884, 340–341). A paper by G. Marpmann (*Ar. Ph.* [3] 20, 905–924) deals with the methods for determining the vitality of those bacteria which cease to move when dead, and points out the difference between antisepsis and disinfection, and gives a list of the literature on the subject to 1881.

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S. R.

FERRATES. Salts of the hypothetical *ferric acid* H_2FeO_4. Neither the acid nor its anhydride (FeO_3) has been isolated.

Stahl noticed in 1702 that a violet solution is obtained by fusing iron with saltpetre and washing with water, or by adding a solution of iron in HNO_3 to conc. KOHAq.

From measurements of the O evolved and the Fe_2O_3 formed in the decomposition of K ferrate, Fremy gave the formula FeO_3 to the hypothetical acidic radicle of the ferrates; this was confirmed by H. Rose, who determined the quantity of I set free from KI by reaction with Ba ferrate (*A.* 48, 230).

The ferrates have been examined by Fremy (*C. R.* 12, 23; 14, 442; 15, 1106; 16, 187); H. Rose (*A.* 48, 230; *P.* 59, 315); Denham Smith, (*P. M.* [3] 23, 217); Merz (*J. pr.* 101, 269); Poggendorff (*P.* 54, 373).

Barium ferrate, $BaFeO_4.H_2O$, has been obtained as a solid. The compositions of the soluble K and Na ferrates were deduced from estimations of the ratio of Fe ppd. as Fe_2O_3 to O evolved by decomposing the solution by heat (Fremy, Denham Smith), and also by reducing by SO_2 and then estimating the ratio of Fe_2O_3 ppd. to SO_4 in solution (H. Rose).

Barium ferrate $BaFeO_4.H_2O$. Obtained as a purple-red powder by adding $BaCl_2Aq$ or $Ba(NO_3)_2Aq$ to K_2FeO_4Aq, washing, and drying (Denham Smith). It is more stable than K_2FeO_4; decomposed by HNO_3Aq, slowly by H_2SO_4Aq; sol. in acetic acid, forming a red liquid, which evolves O on heating; scarcely decomposed by organic salts.

Potassium ferrate, K_2FeO_4Aq. Prepared by heating 2 pts. KNO_3 in a large Hessian crucible, arranged so that only the bottom is heated to dull redness, and throwing in 1 pt. iron filings; the fused mass is extracted with cold water in a closed vessel (Fremy). More conveniently prepared by passing a rapid stream of Cl into conc. KOHAq warmed to about 40°, holding FeO_3H_3 in suspension; Merz (*l.c.*) recommends to dissolve 5 pts. KOH in 8 pts. H_2O, and to add 8 pts. $FeCl_3Aq$ of S.G. 1·109; excess of Cl must be avoided. According to Fremy, crystals of K_2FeO_4 may be obtained by making the KOHAq very conc., and adding KOH from time to time as the Cl is passed in; the crystals may be freed from KCl by solution in water and ppn. by potash, they may then be dried on a porous tile and kept in sealed tubes. Poggendorff (*l.c.*) says that crystals of potassium ferrate may be obtained by an electrolytic method; a cylindrical vessel of porous porcelain is placed in a beaker cooled by ice; potash solution is poured into both vessels, a Pt plate, which serves as negative electrode, is immersed in the porous cylinder, and the positive electrode is a plate of wrought iron (not steel) which is placed in the beaker; when a strong current is passed, the liquid round the positive pole becomes dark red, and crystals of K ferrate form on the iron plate. Bloxam (*C. N.* 54, 43) says that a solution of K_2FeO_4 may be obtained by adding a fragment of KOH to a little Fe_2Cl_6 and then a few drops of Br, heating gently and dissolving in water.

A conc. solution of K_2FeO_4 is deep red; it is stable especially if a little KOH be present; on dilution and warming, FeO_3H_3 is ppd., and O is evolved; the solution is decomposed by acids; it reacts towards SO_2Aq, &c., as an oxidiser; the solution is decolourised by metals and many salts of earth-metals, *e.g.* alum; it is also decolourised by NH_3Aq with evolution of N; the solution acts as an oxidiser towards most organic compounds which are oxidised by $KMnO_4Aq$, *e.g.* alcohol, sugar, albumen, potassium tartrate and oxalate.

Sodium ferrate Na_2FeO_4Aq. Solution obtained similarly to K_2FeO_4Aq.

M. M. P. M.

FERRIC COMPOUNDS *v.* Iron.

FERRICYANIDES and **FERROCYANIDES.** Salts of ferricyanhydric acid H_3FeCy_6, and ferrocyanhydric acid H_4FeCy_6, *v.* pp. 333, 337.

FERRITES. Ferric oxide Fe_2O_3 forms compounds with several metallic oxides more basic than itself; these compounds belong to the form $Fe_2O_3.M_2O$ and $Fe_2O_3.MO$, where $M_2 = K_2$ and Na_2, and M = Ba, Ca, Cu, Mg, or Zn; they are analogous in composition to the aluminates (*q.v.* vol. i. p. 141), and may be regarded as metallic derivatives of the hydroxide $Fe_2O_4H_2 (= Fe_2O_3.H_2O)$.

Barium ferrite $BaO.Fe_2O_3 = BaFe_2O_4$. Obtained by List (*B.* 11, 1512), by ppg. $FeCl_3Aq$ by BaOAq, as a brown, magnetic solid.

Calcium ferrite $CaO.Fe_2O_3 = CaFe_2O_4$. Percy (*P. M.* [4] 45, 455) obtained this salt in metal-like lustrous crystals, S.G. 4·693, by heating equal parts of $CaCO_3$ and Fe_2O_3 to white heat for several hours. List (*B.* 11, 1512) obtained the compound as a brown solid by adding CaOAq to $FeCl_3Aq$, washing with CaOAq, and heating (*v.* also Pelouze, *A. Ch.* [3] 33, 5; also Rousseau a. Bernheim, *C. R.* 106, 1726).

Copper ferrite $CuO.Fe_2O_3 = CuFe_2O_4$. A brownish-black, magnetic solid; by adding KOHAq to a mixture of $CuSO_4$ and $FeCl_3$ in quantity sufficient to ppt. all Cu, drying over H_2SO_4 *in vacuo*, and heating (List, *l.c.*).

Magnesium ferrite $MgO.Fe_2O_3 = MgFe_2O_4$. Occurs native as *Magnoferrite.* Obtained by mixing equivalent quantities of $MgSO_4$ and NaOH and adding $FeCl_3Aq$ until the liquid is still slightly alkaline, and heating the pp. strongly (List, *l.c.*). Kraut (*C. C.* 1864. 1088) obtained $Fe_2O_3.6MgO.9H_2O$ by adding 6 equivs. $MgSO_4$ and 1 equiv. of a ferrous salt to excess of KOHAq, S.G. 1·1, boiling for some hours until the pp. was white, and drying at 120°.

Potassium and Sodium ferrites $K_2O(Na_2O).Fe_2O_3 = K_2(Na_2)Fe_2O_4$. Formed by adding Fe_2O_3 to molten K_2CO_3 or Na_2CO_3 (*v.* v. Schaffgotsch, *A. Ch.* 43, 17; Schneider, *J. pr.* 108, 19; List, *B.* 11, 1512). Rousseau a. Bernheim (*C. R.* 107, 240) describe $K_2O.Fe_2O_3$ as transparent, red-brown crystals; obtained by mixing crude K ferrite (best that made by fusing FeO_3H_3 with 4 parts K_2CO_3) with twice its weight of KCl, and heating strongly until most of the KCl is volatilised. Other crystalline compounds of Fe_2O_3 with K_2O and xH_2O were obtained by heating $FeSO_4$ with an equal weight of KCl.

Zinc ferrite $ZnO.Fe_2O_3 = ZnFe_2O_4$. Occurs native as *Franklinite.* Obtained as minute, black, octahedral crystals, which are slightly magnetic, by heating to whiteness for 4 days a mixture of 1 pt. Fe_2O_3, 2 pts. ZnO, and 2 pts. fused H_3BO_3, and treating with dilute HClAq. S.G. 5·132 (Ebelmen, *A. Ch.* [3] 33, 47; *v.* also Daubrée, *C. R.* 39, 153; Reich, *J. pr.* 83, 266; and List, *B.* 11, 1512).

Ferrites of lead, manganese, and silver seem also to exist (*v.* List, *l.c.*; H. Rose, *P.* 101, 323; Fischer, *S.* 56, 361).

M. M. P. M.

FERULIC ACID $C_{10}H_{10}O_4$ *i.e.* [3:4:1]$C_6H_3(OMe)(OH).CH:CH.CO_2H$. Mol. w. 194. [169°]. Occurs in asafœtida, from which it is obtained by ppg. the alcoholic tincture with lead acetate and decomposing the resulting lead salt by H_2SO_4 (Hlasiwetz a. Barth, *A.* 138, 64). Obtained also by boiling its acetyl derivative with aqueous KOH. Long trimetric four-sided needles (from boiling water). V. sl. sol. cold water, v. sol. cold alcohol, m. sol. ether. Its aqueous solution is ppd. by $Pb(OAc)_2$ and by Fe_2Cl_6. Ammoniacal $AgNO_3$ gives an egg-yellow pp.; reduction takes place on boiling. Potash-fusion gives protocatechuic and acetic acids. It reduces boiling Fehling's solution. Sodium-amalgam reduces it to hydroferulic acid $C_6H_3(OMe)(OH).CH_2.CH_2.CO_2H$ [90°].

Salts.—$NH_4A'aq$: laminæ.—KA′ (at 110°); straw-yellow deliquescent crystals.—AgA′.

Acetyl derivative $C_6H_3(OMe)(OAc).CH:CH.CO_2H$. [197°]. Prepared by boiling a mixture of acetyl-vanillin (5 pts.), NaOAc (5 pts.) and Ac_2O (15 pts.) for 5 hours (Tiemann a. Nagai, *B.* 11, 650). Vanillin may be used instead of its acetyl derivative. Slender needles, v. sol. alcohol and ether, sl. sol. water.

Iso-ferulic acid $C_{10}H_{10}O_4$ *i.e.* [4:3:1] $C_6H_3(OMe)(OH).CH:CH.CO_2H$. *Hesperetic acid.* [228°].

Formation.—1. By the action of MeI and KOH on caffeic acid (Tiemann a. Nagai, *B.* 11, 654).—2. Together with phloroglucin by boiling hesperetin with dilute NaOH.

Properties.—White needles or plates. Sol. alcohol, ether, and hot water, sl. sol. cold water, benzene, and chloroform, insol. ligroïn.

Reactions.—1. Fused with KOH it gives protocatechuic acid.—2. By reduction it gives hydro-isoferulic acid [146°]. On heating it gives CO_2 and hesperetol $\{C_6H_3(OMe)(OH).CH:CH_2\}$.

Salts.—$A'_2Ca\,2aq$: sparingly soluble needles.—A′Ag: slightly sol. pp. The salts of barium, zinc, copper, and lead are also sparingly soluble pps.

Methyl ether A′Me. [79°]. Colourless needles. Soluble in alcohol.

Acetyl derivative $C_6H_3(OMe)(OAc).CH:CH.CO_2H$. [199°]. Colourless plates. Soluble in alcohol and ether, insoluble in water. On oxidation with $KMnO_4$ it gives isovanillic acid.

Methyl-isoferulic acid $C_6H_3(OMe)_2.CH:CH.CO_2H$. *V.* Vol. i. p. 659 (Tiemann a. Will, *B.* 14, 955).

FERULIC ALDEHYDE $C_{10}H_{10}O_3$ *i.e.* [3:4:1]$C_6H_3(OMe)(OH).CH:CH.CHO$. [84°]. From its glucoside by treatment with emulsin at 35° (Tiemann, *B.* 18, 3484). Yellow needles. Sl. sol. cold water, v. sol. alcohol, ether, and benzene; insol. ligroïn. Combines with $NaHSO_3$. Its aqueous solution is coloured green by $FeCl_3$, and on boiling with $FeCl_3$ gives off an odour of vanilla.

Glucoside $C_{16}H_{22}O_8$ *i.e.* $C_6H_3(OMe)(O.C_6H_{11}O_5).CH:CH.CHO$. [202°]. From the glucoside of vanillin by treatment with aqueous NaOH and aldehyde (T.). Yellow needles (containing 2aq) (from water). Sl. sol. cold water, v. sol. alcohol, insol. ether, chloroform, and benzene. Lævorotatory.

Oxim of the glucoside $C_6H_3(OMe)(OC_6H_{11}O_5)CH:CH.CH:NOH$. [163°]. Needles, sl. sol. cold water, m. sol. alcohol, insol. ether.

Phenyl hydrazide of the glucoside $C_6H_3(OMe)(OC_6H_{11}O_5).CH:CH.CH:N_2HPh$. [212°]. Amorphous, v. sol. alcohol. v. sl. sol. water and ether.

FIBRIN *v.* Proteids and Blood.

FIBRINOGEN *v.* Proteids.

FIBRINOPLASTIN *v.* Proteids.

FIBROIN *v.* Proteids, *Appendix C.*

FICHTELITE $C_{15}H_{26}$ or $C_{15}H_{28}$. [46°]. (above 320°). A fossil resin found in the Fichtelgebirge. It is a hydro-carbon containing from 87 to 88 p.c. carbon (Trommsdorff, *A.* 21, 126; Bromeis, *A.* 37, 304; Clark, *A.* 103, 236; 119, 226; Schrötter, *P.* 59, 37; Hell, *B.* 22, 498). Monoclinic prisms. Insoluble in, and lighter than, water; v. sl. sol. alcohol, v. e. sol. ether. With halogens it gives products by substitution.

FILICIC ACID $C_{14}H_{16}O_5$. *Isobutyryl-oxy-naphtho-quinone?* [180° uncor.]; [185°] (L.). Occurs in the root of the common male fern (*Aspidium Filix-mas*) from which it may be extracted by dry ether. After a few days the ether deposits the acid as a greenish-yellow powder, which may be purified by washing with alcohol-ether and recrystallising from ether (Luck, *A.* 54, 119; *B.* 21, 3465; Grabowski, *A.* 143, 279; Daccomo, *C. C.* 1887, 1357; *B.* 21, 2962; Paternò, *B.* 22, 463). Minute laminæ, insol. water, v. sl. sol. alcohol, sl. sol. ether, v. e. sol. CS_2, ligroin, and terpenes. After fusion it melts at 150° to 160°. Its solution reddens litmus. Potash-fusion gives butyric acid and phloroglucin. Water at 180° gives isobutyric acid and a body $C_{20}H_{18}O_7$. $KMnO_4$ and HNO_3 (S.G. 1·4) give isobutyric and oxalic acids. Zinc dust gives a body $C_{14}H_{22}O_{11}$.—PbA'_2: curdy pp.

Benzoyl derivative $C_{21}H_{20}O_6$. [123°]

Ethyl ether [142°]. Brick-red crystals.

Ethylene ether. [165°].

Propyl ether. [158°].

Phenyl-hydrazide $C_{14}H_{16}O(N_2HPh)_4$. [198°]. Red needles (from ether).

Anilide $C_{14}H_{15}O_4NHPh$. [140°].

Bromo-filicic acid $C_{14}H_{15}BrO_5$. [122°].

Chlorofilicic acid $C_{14}H_{15}ClO_5$. From chlorine gas and solid filicic acid. Amorphous. Its alcoholic solution gives with lead acetate a pp. of PbA'_2.

Tri-chloro-filicic acid $C_{14}H_{13}Cl_3O_5$. Formed by the action of chlorine on filicic acid suspended in water. Amorphous.—PbA'_2.

FILTRATION. The separation of a solid from a liquid by means of a membrane impervious to the solid.

FISCIC ACID. C. 67·33 to 67·66; H. 4·73 to 5·08. [204°]. A substance extracted from the *Fiscia parietina*, a lichen growing abundantly in Sicily on the branches of shrubs. Prepared by heating the lichen in a reflux apparatus with boiling alcohol; the black residue on treatment with ether leaves a black crystalline residue, which is frequently recrystallised from benzene in presence of animal charcoal. Yield small. Forms red-brown crystals, soluble in potash forming a rose-red salt. It exhibits considerable resemblance to chrysophanic acid, but differs from it in composition and higher melting-point (Paternò, *G.* 1882, 254).

FISETIN $C_{23}H_{16}O_9$ (J. Schmid, *B.* 19, 1734; *cf.* Koch, *B.* 5, 285; Bolley, *Bl.* [2] 2, 479). This name was given by Chevreul to 'young fustic,' the yellow colouring matter of Fiset wood (the heart-wood of *Rhus Cotinus*, a species of sumach). It occurs as a glucoside combined with a tannin. Alkalis or acids split this compound up into the tannin and the glucoside ('fustin'). The glucoside is split up by dilute H_2SO_4 into fisetin and a sugar. Fisetin crystallises from alcohol in small lemon-yellow prisms; and from HOAc in yellow prisms (containing 6aq). Sl. sol. ether, benzene, ligroïn, chloroform, and boiling water, v. sol. alcohol. It begins to blacken at 270° but does not melt below 360°. It may be sublimed in small needles. Nitric acid oxidises it to oxalic and picric acids. H_2SO_4 forms a sulphonic acid. It reduces Fehling's solution. Alkalis turn its alcoholic solution brownish-red. Potash-fusion gives protocatechuic acid and phloroglucin.

Salt.—$C_{23}H_{14}Na_2O_9$: yellow needles.

Acetyl derivative $C_{23}H_{10}Ac_6O_9$. [201°]. Needles, sl. sol. boiling alcohol, v. sol. chloroform.

Benzoyl derivative $C_{23}H_{10}Bz_6O_9$. [185°]. Needles. With excess of BzCl it gives a compound [195°].

Glucoside $\{(C_6H_{11}O_6).C_{23}H_{12}O_5\}_2O$. *Fustin.* [219°]. Obtained as above. Needles; v. sol. boiling water, alcohol, and alkalis, sl. sol. ether. Lead acetate gives a yellow pp. Cupric acetate gives a brown pp. $FeCl_3$ produces a green colour which, on addition of dilute soda, changes through violet-blue to red.

Ethyl derivative $C_{23}H_{10}Et_6O_9$. [107°]. Long pale-yellow needles.

Methyl derivative $C_{23}H_{10}Me_6O_9$. [153°].

FIXED AIR. The name given by Black to carbonic anhydride CO_2 (*v.* vol. i. p. 691).

FLAME is gas or vapour raised to a temperature at which it becomes self-luminous. The luminosity depends essentially on the specific emissive power for light of the incandescent gas, and according to the law of exchanges is proportioned to the power of the gas to absorb the same kind of light at the same temperature. In nearly all cases, the high temperature, and hence the flame, is the result of chemical energy, displayed (in the great majority of instances) in the combination of two or more gaseous substances; hence the production of flame is in general essentially a synthetical process. There are, however, cases in which flame is produced by the breaking up of a complex molecule either into simpler forms of combination, or into its elements, as, for example, in the flame which accompanies the destruction of nitrogen trichloride where no combination or rearrangement of the constituent elements other than into molecules takes place. Flames of this character are invariably 'solid,' *i.e.* they are wholly composed of glowing particles, and are wanting in the internal structure which is characteristic of all ordinary flames. Flames of the synthetical class may, however, be 'solid'—such, for example, are the flames of intimate mixtures of oxygen and hydrogen, of chlorine and hydrogen, or of vapour of carbon disulphide and nitric oxide. In these cases the chemical combination is exceedingly rapid; the heat developed is great, and the consequent molecular vibration is so intense that it becomes explosive in character.

According to Bunsen (*P. A.* 131, 161) in a mixture of carbon monoxide, or hydrogen, with oxygen in the exact quantity needed for complete combination, only one-third of the carbon monoxide or hydrogen is burnt at the maximum temperature, the remaining two-thirds at the high temperature (2558°–3033°) having lost the power of combination. If an indifferent gas is present the temperature of the flame is reduced, and larger quantities of the gases combine together, as much as half the amount of carbon monoxide or hydrogen combining within a range of temperature between 2471° and 1146°.

It would appear, therefore, that gases in combining together with the production of such an amount of heat as to produce flame unite *per saltum*, and that the combustion is not a continuous uninterrupted process. Thus in the case of carbon monoxide, when two vols. of this gas are mixed with one vol. of oxygen, both gases at 0°, and the mixture is ignited, the temperature is raised to 3033°, and two-thirds of the carbon monoxide is left unburnt; by radiation and conduction the temperature is lowered to 2558° without any combustion of the carbonic oxide; at a little below this point combustion recommences, and the temperature is again raised to 2558°, but not above this point. This temperature continues until half the carbon monoxide is burnt, when the combustion ceases, until by cooling and radiation the gaseous mixture has cooled to 1146°, and these alternate phases of constant temperature and of decreasing temperature are repeated until the whole of the combustible gas is burnt.

Bunsen has also determined the rate of propagation of the combustion of a mixture of oxygen and hydrogen, and of carbon monoxide and oxygen, mixed in the exact quantities for complete combustion. In the oxyhydrogen mixture the velocity of inflammation was 34 metres per second; in that of carbon monoxide and oxygen it was less than 1 metre per second. By adding to the mixture increasing amounts of an indifferent gas the rate is rapidly diminished until the progress of the flame throughout the mass may be followed with the eye.

The flames with which we are ordinarily familiar, as that of a candle or of coal-gas, are, however, of a very different character from the so-called 'solid' flames. In ordinary flames a stream of combustible gas comes in contact with atmospheric air at a temperature sufficiently high to effect the chemical union of the constituents of the gas with the oxygen of the air with the consequent production of heat and light. It is obvious that this union can only take place at the points of contact between the air and the gas: hence such a flame is necessarily hollow, its internal space consisting of 'combustible' gas which has not yet come into contact with oxygen in quantity sufficient to burn it. The form of the flame for any particular gas will therefore be dependent upon the mode in which the gas is caused to issue into the air, and this, in its turn, is controlled by the character of the jet or burner, and by the pressure under which the gas is delivered.

It is obviously immaterial so far as the production of a flame is concerned whether the gas issues into the oxygen, or the oxygen into the 'combustible' gas. In either case we shall have chemical combination occurring at the point of contact of the two gaseous substances, provided the temperature be raised to that of ignition, and a flame will result from the heat of combination. In this way chlorine may be caused to burn in hydrogen, and air may seem to burn in coal-gas. Hence the terms 'combustible' and 'supporter of combustion' as applied to gases which may be made to burn in each other have no real significance; the same gas may appear to be 'combustible,' or 'to support combustion,' in accordance with the manner in which it is presented to the gas with which it combines with the production of sufficient heat to give flame.

The two main factors which determine the interaction of two gases, which are susceptible of chemical change when mixed, are temperature and degree of condensation. A stream of hydrogen issuing into the air under ordinary circumstances does not ignite. If, however, the air or the hydrogen, or both, be raised to a sufficiently high temperature just prior to admixture, chemical union will be initiated and flame will result. Hence a red-hot wire, or the flame of a taper, or electric sparks, cause the hydrogen to burn; these means have sufficed to raise the temperature of the gases to the point at which chemical combination can occur. The union of oxygen and hydrogen may, however, be effected at a low temperature under certain conditions, as, for example, by the 'catalytic' action of platinum or palladium. If a perfectly clean piece of palladium or platinum foil be suspended in a mixture of oxygen and hydrogen at the ordinary temperature, water will be seen to form on the surface of the metal in rapidly increasing quantity, the metal will become hot and will eventually raise the temperature of the gases to the point at which an almost instantaneous combination will occur, and flame and explosion will result. This power to effect union is dependent on the capacity of the metal to 'occlude' gas, and, as Berliner (*W.* 35, 791) has shown, it is more efficacious in the case of palladium than in that of platinum, in conformity with Graham's observations of the relative 'occlusive' capacities of the two metals for hydrogen. The 'catalytic' action is greatly augmented by increase of temperature, which explains the rapidly increasing rate of formation of water and the eventual explosion. The occluded hydrogen at the ordinary temperature combines with oxygen, heat is developed, and this accelerates the union of fresh quantities of the gases, the metal is thereby rapidly raised in temperature, and eventually brings the mixture to the point of inflammation. Precisely the same principle is seen at work in the well-known Döbereiner lamp, in which a current of hydrogen is caused to impinge upon a small quantity of platinum-black which has been exposed to the air. Under the influence of the finely divided metal the gases combine with the generation of sufficient heat to effect the ignition of the hydrogen as it issues into the air. Dulong and Thenard, and Turner and Henry, have shown that copper and iron turnings, zinc foil, and even charcoal, will bring about the same result, although much less actively, at varying temperatures up to the boiling-point of mercury.

Certain gases and vapours spontaneously inflame as they issue into the air, such, for example, are boron and silicon hydrides, the dihydride of phosphorus, thio-phosphoryl fluoride, cacodyl, zinc-ethyl, &c. Thus too acetylene spontaneously inflames in chlorine, and sulphuretted hydrogen in chloric oxide. The spontaneous inflammation may in some cases be due to the fact that the ignition-temperature of the mixture is as low as that of the ordinary temperature of the air, or that the temperature has been raised to the ignition-point by a preliminary reaction between the substances. The spontaneous inflammation of 'engine-waste,' or wool saturated with oil, is due, in the first instance, to the development of heat attending the absorption of oxygen from the air by the oil. Oxygen so absorbed by oil will indeed act as energetically as if occluded by platinum. A woollen rag or a bit of blanket sprinkled with oil and suspended in a mixture of sulphur dioxide and air will rapidly 'tinder' from the formation of oil of vitriol.

We have as yet no very exact information concerning the ignition-temperatures of gases. The experimental difficulties in the way of carrying out such determinations are very considerable. A. Mitscherlich has described a method (*Fr.* 16, 67) of ascertaining the ignition-point, but no determinations by means of it have yet been published. It is, however, certain that the ignition-temperatures of gaseous mixtures are as a rule by no means so high as is commonly supposed, and they lie within extremes of temperature admitting of comparatively easy determination. When once initiated, the continuance of the combination of unlimited amounts of the constituents of a combustible mixture, or in other words the continued existence of a flame, depends primarily upon the condition that the combining gases are maintained at the temperature required to bring about their union. Any agency or condition which lowers the temperature below this point will extinguish the flame. A coal-gas flame is extinguished by a cold mass of copper, and a candle flame by a helix of cold copper wire. The metal abstracts sufficient heat from the gases to lower their temperature below the point of combination. If the metal is heated prior to its introduction into the flames they are not extinguished.

The cooling action of metal is made use of in the Hemming safety-jet used for burning mixtures of oxygen and hydrogen, but a far more important application of it is seen in the Davy safety-lamp. This is simply a small oil-lamp surrounded by a cylinder of wire gauze. If the lamp is introduced into an explosive mixture of fire-damp and air, combination occurs within the cylinder, but the flame is prevented from traversing the gauze by the cooling action of the metal. Any circumstance which causes the gauze to become hot, or which prevents it from exerting its specific cooling action, renders the lamp unsafe. Thus if the flame impinges on the wire gauze so as to heat it to redness, or if the burning lamp be held in a current of air and fire-damp exceeding in velocity six feet per second, or if it be struck by a sound wave of sufficient intensity, the flame will pass through the meshes, and may ignite an explosive mixture on the outside of the cylinder.

A flame may be extinguished, however, in other ways than by the cooling action of metals, as, for example, by mixing the combustible gases with a sufficiently large quantity of an indifferent gas which will act by absorption of heat, in the same way as metal. The effect even of small quantities of indifferent or chemically inactive gases in lowering the temperature of a flame is very marked, and is well illustrated in the different characters of the flame of hydrogen burning in air and in oxygen. In extinguishing a flame, say of a candle or coal-gas, by 'blowing it out,' the puff of air acts partly by suddenly scattering the glowing gases from the area of supply and partly by its cooling action. Although oxygen is essential to the existence of the oxyhydrogen flame, it is readily possible to extinguish the flame by an excessive supply of that gas within the jet. The power which an indifferent gas possesses in destroying flame has received important practical applications in several fire-extinguishing apparatuses.

If the flame of a candle or of coal-gas be closely examined it will be seen that the one does not touch the rim of the burner nor the other the wick (Blochmann, *A.* 168, 345). The intermediate space in the case of coal-gas may be increased by mixing it with an indifferent gas, as nitrogen or carbon dioxide. These phenomena are due to the cooling effect of the wick or the burner. Whenever a cold object touches a flame, a dividing space, similar to that noticed between flame and burner, is observed, the size of which is dependent on the coldness of the object or its specific heat, and the dilution of the burning gas. A thick metallic wire, brought into a flame diluted with carbon dioxide, causes a clear space around itself, which increases with the proportion of the indifferent gas. The diluting gas lowers the temperature of the flame, by diffusing the heat needed to maintain a given quantity of the coal-gas in a state of combustion throughout a greatly increased volume of gas. If the temperature of the flame is already low, the further decrease resulting from the introduction of the cold object suffices to cool a comparatively large extent of gas below the ignition-point, and hence to extinguish the flame in the cooled space.

Rarefaction of the gases prevents the continuance of combustion by retarding combination, whereby the temperature of the gases sinks below that necessary to effect union. A jet of hydrogen issuing into rarefied air gives at first an increased size of flame, but it ceases to burn when the air is rarefied to $\frac{1}{8}$th its ordinary pressure, and a mixture of 2 vols. of hydrogen and 1 vol. of oxygen is not explosive when rarefied to $\frac{1}{18}$th its ordinary density. By mixing oxygen with an indifferent gas many phenomena of combustion are immediately arrested, unless some extrinsic agency is at work to maintain or even raise the temperature. The combustion of iron wire in oxygen stops almost immediately when the glowing metal is withdrawn into the air.

On the other hand, instances are known in which sudden rarefaction will produce spontaneous ignition even at the ordinary temperature. Thus pure phosphine mixed with oxygen is not spontaneously inflammable at ordinary temperatures and pressures, but on suddenly expanding the mixture it inflames with explosive violence. In the same way thiophosphoryl fluoride, if mixed with an indifferent gas and thereafter with oxygen, will detonate on a sudden diminution of the pressure. These phenomena are in all probability connected with the extreme instability of these gases, and are akin to the cases of decomposition by shock which have been studied by Berthelot and others (*v.* EXPLOSION).

It has already been stated that the *form* of a steady continuous flame depends upon the mode in which the combustible gas issues into the air, and this is dependent upon the form and size of the jet, or, in the case of a candle, of the wick. The *size* of the flame from gas issuing at a constant rate is dependent on the temperature, pressure, and relative diffusibilities, of the combining substances. By increasing the amount of oxygen in the air the size of a flame may be considerably diminished. This fact is well illustrated by plunging a jet of hydrogen burning under constant pressure in air into oxygen gas. The increased size of the flame under ordinary conditions is due to the fact that the air contains only one-fifth of its volume of oxygen; the 'combustible' gas has to seek, therefore, over a larger area for the oxygen required for combination. The size of a flame is also necessarily determined by the volume of oxygen needed for the complete combustion of the inflammable gas. Thus equal volumes of hydrogen and of ethylene passing through the same jet and at the same rate into oxygen will give flames of very different size: the hydrogen, which needs only half its volume of oxygen to burn it, forms a much smaller flame than the ethylene, which requires three times its volume. On the other hand, oxygen burning in hydrogen gives a larger flame than when burning in marsh gas; in the former case the oxygen needs 2 vols. of hydrogen for its combustion; in the latter only half a volume of marsh gas.

The *temperature* of flames is extremely variable. Some, like that of sulphur burning in air, are comparatively low; others furnish us with some of the highest temperatures of which we have any practical knowledge. The temperature of a flame depends mainly upon the heats of combination of the constituents and the specific heats of the products of combustion. Flames which depend upon the presence of oxygen are much hotter when the combustion takes place in an atmosphere of the pure gas than in air. In the latter case the oxygen is mixed with four times its volume of nitrogen, which plays no part in the chemical reaction, and therefore contributes nothing to the heating effect, but on the contrary abstracts a considerable amount of heat from the products of combustion, and thereby lowers the temperature of the glowing mass of gas. Hence sulphur burning in oxygen gives a much hotter flame than when burning in air, and the oxyhydrogen flame is much hotter than that of hydrogen in air. The effect of the indifferent gas in lowering the temperature is well illustrated by the following numbers given by Bunsen (*P. M.* [4] 34, 489).

Flame of hydrogen burning in air	2,024°
„ „ „ oxygen	2,814°
„ carbonic oxide burning in air	1,997°
„ „ „ oxygen	3,003°.

The conditions under which a flame is produced not only modify its temperature, but also, as an effect of temperature, its *colour*. Thus the prevailing tint of sulphur burning in air is blue, and the mantle is comparatively small and of a violet colour. In oxygen the flame becomes hotter, and the violet colour is more pronounced. Precisely the same change is produced by heating the air or by burning a jet of heated sulphur vapour. Cold carbonic oxide gives a blue flame in air, but it becomes yellowish-red if the gas be previously heated.

The flame of a candle, whether of wax, tallow, or paraffin, is seen to consist of four distinct cones, which are comparatively sharply defined, and which are rendered evident by their different appearance. Immediately surrounding the wick is a dark inner cone consisting of unburnt gases or vapours distilled from the fatty matter raised by the capillary action of the wick from the reservoir of melted material at its base. Below the inner cone is a light-blue zone of small area consisting of combustible matter from the wick, which has become mixed with an amount of oxygen sufficient to burn it completely to non-luminiferous gases. Surrounding the inner cone is a bright luminous area, from which the greater part of the light emitted by the flame is derived. This area constitutes the main meeting-place of the combustible gases with the oxygen, and hence chemical combination is here most vigorous. Surrounding the luminous area, which seems to constitute the greater portion of the visible flame, is an envelope or mantle of a faint yellowish colour and of feeble luminosity; this consists of the final products of combustion of the constituents of the luminous cone mixed with atmospheric air heated to incandescence. Owing to the intense glare of the luminous cone the feebly luminous mantle is not readily perceived, but it may be rendered evident by holding a piece of card of the shape of the flame in such a manner as to hide the luminous cone, when the mantle is seen lining the outer edge of the cone. The fact that the candle flame is hollow, and that the internal cone immediately surrounding the wick consists of comparatively cold unignited gas free from oxygen, may be demonstrated by thrusting a fragment of burning phosphorus into the cone, when its combustion ceases. A piece of stiff thick paper thrust down on the flame to the level of the dark internal area is seen to be charred on the upper surface in the form of a ring; if the paper be placed simply across the luminous area and above the dark cone the charring is simply a circular patch.

In other steady, continuous flames these areas or zones are very different in character and in number. In some the luminous cone is absent, and others have no mantle; all have, of course, the dark internal cone, and the majority have an area corresponding to the blue zone in the candle flame. In an alcohol flame the internal cone is large, owing probably to the ready volatilisation of the combustible vapour; the luminous cone is small, and the mantle seems to be largely developed. The flame of carbon monoxide consists of a dark internal cone of unburnt gas surrounded by a yellowish-red mantle somewhat ill-defined at its external edge, and at the base is a comparatively large blue zone.

Attempts have been made by Hilgard (*A.* 92, 129), Landolt (*P. A.* 99, 389), Blochmann (*A.* 158, 295), and others, to study the nature of the chemical process in flames of candles and of coal-gas, by aspirating the gases from different parts of the flame and analysing them. Such investigations can only give a very partial conception of the changes which occur or have occurred in the different areas of the flame owing to the intense molecular movements, due to the high temperature and specific differences of diffusive power, of the gaseous constituents. Nevertheless it is possible to obtain some idea of the manner in which the several combustible gases in such a complex mixture as that of coal-gas, or of the gas obtained by the distillation of wax or tallow, behave towards oxygen, and to trace the rates at which they are severally burnt. Thus, broadly speaking, it is found that of these gases, the hydrogen up to a certain point is most rapidly consumed, then the carbonic oxide, next the marsh gas, while the heavy hydrocarbons burn comparatively slowly. The amounts of these gases burnt, and especially of the hydrogen and carbonic oxide, are, however, modified by processes of dissociation, and by the mutual action of the products of combustion at high temperatures; at very high temperatures water vapour and carbon dioxide are dissociated, while carbon monoxide is formed by the action of separated carbon upon carbon dioxide. The process of breaking up the hydrocarbons is one of gradual degradation, the higher members of the paraffin series being probably resolved into olefines and paraffins of lower molecular weight:

$$C_{n+p}H_{2n+2p+2} = C_nH_{2n+2} + C_pH_{2p},$$

as in the case of butane, which is known to be resolved into ethane and ethylene, $C_4H_{10} = C_2H_6 + C_2H_4$. At a sufficiently high temperature ethylene is further broken up as follows:

$$2C_2H_4 = C_2H_6 + C_2H_2$$
$$2C_2H_4 = 2CH_4 + 2C.$$

On the other hand, at high temperatures marsh gas is known to form naphthalene $C_{10}H_8$ and acetylene; while at still higher temperatures it is resolved into carbon and hydrogen.

The main cause of the luminosity of a candle-flame, and indeed of all our ordinary illuminating flames, was first traced by Davy as the outcome of the experiments which led him to the invention of the safety lamp. It is, to use his own words, 'owing to the *decomposition* of a part of the gas towards the interior of the flame, where the air was in smallest quantity, and the deposition of solid charcoal, which first by its ignition, and afterwards by its combustion, increases in a high degree the intensity of the light' (*Tr.* 1817, 45, 77). The proofs that solid carbon is present in luminous hydrocarbon flames are the following (*v.* especially Heumann, *P. M.* 1877).

1. *Chlorine causes an increase in the luminosity of feebly-luminous or non-luminous hydrocarbon flames.* Since chlorine decomposes hydrocarbons at a red heat with separation of carbon, it follows that the increase in luminosity is due to the production of solid carbon particles.

2. *A rod held in the luminous flame soon becomes covered on its lower surface, i.e. the surface opposed to the issuing gas, with a deposit of soot.* The solid soot is driven against the rod. If the soot existed as vapour within the luminous flame, its deposition would be due to a diminution of the temperature of the flame, and would, therefore, occur on all sides of the rod.

3. *A strongly heated surface also becomes covered with a deposit of soot.* This result could not occur if the deposit were due to the cooling action of the surface.

4. *The carbon particles in the luminous flame are rendered visible when the flame comes in contact with another flame, or with a heated surface.* The separated particles are agglomerated into larger masses, and the luminous mantle becomes filled with a number of glowing points, giving a very coarse-grained soot.

5. *The transparency of a luminous flame is no greater than that of the approximately equally thick stratum of soot which rises from the flame of burning turpentine, and which is generally allowed to contain solid particles.* A flame of hydrogen made luminous with solid chromic oxide, which is non-volatile, is as transparent as the hydrocarbon flame.

6. *Flames which undoubtedly owe their luminosity to finely divided solid matter produce shadows in sunlight.* The only luminous flames incapable of producing shadows are those consisting of glowing gases and vapours.

7. *Luminous hydrocarbon flames produce strongly marked shadows in sunlight; these flames, therefore, contain finely divided solid matter.* This solid matter must be carbon, since no other substance capable of remaining solid at the temperature of these flames is present (Heumann). Moreover, if the soot in luminous flames is present as vapour, a high temperature after condensation should again cause it to assume the gaseous condition, but soot is absolutely non-volatile even at the highest temperatures.

The presence of solid matter is, however, not the sole cause of the luminosity of a candle or hydrocarbon flame, since a small portion of the light is derived from the incandescence of the gaseous matters. Methane, which when burning under ordinary conditions gives no deposit of soot, still affords a flame of considerable illuminating power (equal to 5·2 candles according to Lewis T. Wright, *C. J.* 47, 200). Bright flames may indeed be produced without the intervention of solid matter. Arsenic burns in oxygen with a bright flame, although the product of the combustion (arsenious oxide) is volatile at the temperature of its formation. A mixture of nitric oxide and carbon disulphide burns with a brilliant light although no separation of solid matter occurs. It has already been pointed out that substances burning in oxygen give much hotter flames than when burning in air, and it is also found that the flames in oxygen are much more luminous than those in air. Hence the temperature of a flame very considerably affects its light-giving power. E. Frankland has pointed out the connexion between the luminiferous character of flames and the density of their constituents, as is exemplified by the greater illuminating power of a hydrogen flame in chlorine than in oxygen. The luminosity of a flame is increased by condensing the surrounding atmosphere and diminished by rarefying it. Boyle, in 1658, minutely described the appearance of a candle-flame as seen under diminished pressure in the receiver of his 'new pneumatical engine.' E. Frankland found that candles give much less light when burning at the top of Mont Blanc than in the valley below, although the rate of combustion is not much affected by the difference in the density of the air. The flame of arsenic burning in oxygen is greatly diminished in brightness by rarefying the oxygen, and the flame of an alcohol lamp increases greatly in luminosity when burning in condensed air. Under a pressure of 10 atmospheres the flames of hydrogen and of carbon monoxide become very bright and give continuous spectra, and an electric spark increases in luminosity with the density of the gaseous medium through which it passes (Frankland, *Pr.* 16, 419).

Similar observations have been made by L. Cailletet (*A. Ch.* [5] 6, 429), who found that the flames of candles, sulphur, potassium, and carbon disulphide, but not of phosphorus, burned in gradually compressed air with continually increasing intensity of illumination up to pressures of 35 atmos. On the other hand, Wartha (*J. pr.* [2] 14, 84) found that the flame of a stearin candle burning in air under a pressure of 1·95 at. is from 13 to 17·4 p.c. less luminous than when burning in air of ordinary density. At the higher pressure candles burn with a dull yellowish-red smoky flame fully twice as long as that of the same candles burning in the open air. Candles burning at a constant pressure of 90 mm. give a large, clear, non-luminous flame, consisting of an inner bluish-green cone, surrounded by a violet zone, and inclosed by a very faint violet mantle. The non-luminosity of flame under low pressures was supposed by E. Frankland to be due to the increased mobility of the oxygen molecules in the rarefied air in consequence of which they were able to penetrate more freely into the interior of the flame. According to Wartha, the difference is to be attributed to the effect of the pressure on the dissociation-point of the burning substance. When candles are burned in air, under very high pressure, the dissociation of the hydrocarbons takes place more rapidly than the products can be burned, and the flame becomes smoky; under reduced pressure the reverse is the case.

A comparatively small admixture of air greatly impairs the illuminating power of coal-gas. Sillimann a. H. Wurtz (*Am. S.* [2] 48, 40) found that on adding varying quantities of air to a coal-gas having an illuminating value of 14·8 candles the loss of light was as follows:

Added air	Percentage loss of light
3·00 p.c.	15·69
4·96 „	23·83
11·71 „	41·46
16·18 „	57·53.

On adding about 25 p.c. of air the illuminating power diminished 84 p.c. With such an admixture coal-gas burns with a smokeless and practically non-luminous flame.

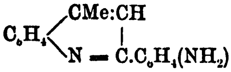
It has been shown that a coal-gas flame burning in air becomes non-luminous by previous admixture with nitrogen, hydrochloric acid, carbon dioxide (Knapp), carbon monoxide, hydrogen (Blochmann), or even steam (Sandow). P. F. Frankland found that while the illuminating power of ethylene was diminished after a certain point by admixture with ordinarily non-luminous combustible gases, the loss of light depended on the nature of the diluent, and was greatest with carbonic oxide and least with marsh gas. An admixture of the combustible gas up to 40 p.c. hardly affects the illuminating power of the ethylene (*C. J.* 45, 39). Mixtures of oxygen with ethylene in quantity insufficient to form an explosive mixture possess a greater illuminating power than pure ethylene. By the addition of carbon dioxide, nitrogen, or aqueous vapour, the illuminating power of ethylene is diminished. These gases act partly by dilution, and partly by cooling; the cooling action is proportional to the specific heats of the gases, but in the case of carbon dioxide and aqueous vapour it is augmented by the absorption of heat which takes place in the dissociation of the aqueous vapour, and in the reduction of the carbon dioxide to carbon monoxide (P. F. Frankland, *C. J.* 45, 236).

Wibel has shown that a mixture of coal-gas and air, which when burnt under ordinary conditions is non-luminous, may be made to give a luminous flame if it is heated previous to inflammation (*B.* 8, 226); and Heumann (*A.* 181, 129; 182, 1; 183, 102; 184, 206) has proved that the luminosity is actually due to the added heat, and not to any alteration in the composition of the gaseous mixture in consequence of the heating.

These observations have an important bearing on the theory of the flame of the Bunsen lamp. The nature of the chemical changes in this flame has been studied by Blochmann (*A.* 168, 295). The feebly luminosity of the Bunsen flame is due (1) to a rapid oxidation of luminiferous material to gases of feebly illuminating power by the oxygen in the admixed air; (2) to the presence of diluting gases which of themselves reduce the illuminating power; and (3) to the heat withdrawn by the indifferent gases, as nitrogen, and the products of combustion, carbon dioxide and water. The loss of luminosity is not due to any one of these causes acting singly. A flame of mixed coal-gas and air has a higher temperature than that of the undiluted coal-gas, but it requires a still higher temperature in order that a separation of carbon shall occur.

When the flame of a Bunsen lamp retreats down the tube and burns at the jet at the bottom a much smaller quantity of air passes into the tube. Under normal conditions 1 vol. of the gas becomes mixed with about 2½ vols. of air: when burning at the bottom the gas becomes mixed with only about 1¼ vols. of air. The effect of this diminished amount of air is a large increase in the amount of carbon monoxide, together with the production of notable quantities of acetylene, to which substances the extremely disagreeable nature of the gases evolved from the burner under these circumstances is due. (Compare Thorpe 'On the Theory of the Bunsen Lamp,' *C. J.* 1877. 1, 627.) T. E. T

FLAVANILINE $C_{16}H_{14}N_2$ *i.e.*



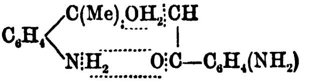
$$C_6H_4\left\langle\begin{array}{l}CMe{:}CH\\ \quad|\\ N=C.C_6H_4(NH_2)\end{array}\right.$$

[1:4]. *p-Amido-(Py.3)-phenyl-(Py.1)-methyl-quinoline.* [97°].

Formation.—1. By heating equal mols. of ortho- and para-amidoacetophenone with an equal weight of zinc-dust at 50°-100°; the yield is 50 p.c.—2. By nitration and reduction of flavoline. 3. By heating *o*-amido-acetophenone to 230° with $ZnCl_2$.—4. By the action of acetyl chloride on aniline sulphate.

Preparation.—By heating acetanilide with $ZnCl_2$ for several hours at 250°-270°, the melt is dissolved in boiling dilute HCl, sodium acetate added, and the product salted out (O. Fischer a. Rudolph, *B.* 15, 1500).

Theory of formation from acetanilide. At the temperature employed the acetanilide undergoes isomeric change, being converted into a mixture of *o*- and *p*-amido-acetophenone, and the latter (as shown in *formation* 1) gives the dyestuff by the elimination of $2H_2O$ from two mols. by means of the $ZnCl_2$:



$$C_6H_4\left\langle\begin{array}{l}C(Me)\,OH_2\,CH\\ \qquad\qquad\quad|\\ N\,H_2 \quad O\,C—C_6H_4(NH_2)\end{array}\right.$$

(Besthorn a. O. Fischer, *B.* 16, 68).

Constitution.—Contrary to the earlier supposition, flavaniline has the NH_2 group in the *para-* position not in the *ortho-*. The fact that a small quantity of the dyestuff is formed by heating *ortho*-amido-acetophenone with $ZnCl_2$ at 250° must be due to an isomeric change of a portion of the *o*-amido-acetophenone into *p*-amido-acetophenone.

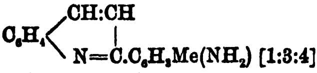
Properties.—Long colourless needles. Distils undecomposed at a high temperature. Sol. alcohol, insol. water. Strong di-acid base. The salts form a splendid yellow dyestuff of green fluorescence. By the action of nitrous acid it yields flavenol.

Salts.—$B''H_2Cl_2$: colourless soluble needles. —$B''HCl$: yellowish-red soluble prisms. —$B''H_2Cl_2PtCl_4$: sparingly soluble crystalline pp.

Reactions.—It cannot be reduced to a hydride by tin and HCl; but on treatment with alcohol and sodium it yields a fluid base, the salts of which are colourless, and forms a crystalline nitrosamine. Heated with glycerin, nitrobenzene and H_2SO_4 it yields a methyl-diquinoline [138°] (O. Fischer, *B.* 19, 1036).

Reference.—*Ethyl-flavaniline.*

Pseudo-flavanilin $C_{16}H_{14}N_2$ *i.e.*



$$C_6H_4\left\langle\begin{array}{l}CH{:}CH\\ \quad|\\ N=C.C_6H_3Me(NH_2)\end{array}\right.$$

[1:3:4]. *Amido-tolyl-quinoline.* [112°].

Preparation. — By leading oxygen over a mixture of quinoline and o-toluidine hydrochloride heated to 180° on platinised asbestos (Weidel a. Bamberger, *M.* 9, 99).

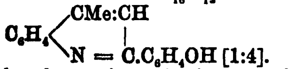
Properties.—Flexible, hair-like needles (from water). Converted by HNO_2 into pseudo-flavenol $C_{16}H_{12}NOH$, which on further oxidation gives quinaldinic acid $C_{10}H_7NO_2$.

Salts.—$B''H_2Cl_2$: long needles.—$B''HCl$: small yellow monoclinic needles.—$B''H_2PtCl_6$.

Acetyl derivative $C_{16}H_{13}AcN_2$. [177°].

FLAVANTHRACENE-DI-SULPHONIC ACID *v.* Anthracene-di-sulphonic acid (*flav-*).

FLAVENOL $C_{16}H_{13}NO$ *i.e.*



$$C_6H_4\left\langle\begin{array}{l}CMe{:}CH\\ \quad\quad\ \ |\\ N = C.C_6H_4OH\end{array}\right.$$

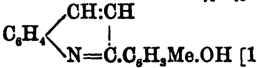
[1:4]. [238°]. Formed by the action of nitrous acid on flavaniline. Sublimable. Colourless iridescent plates. Sol. alcohol and aqueous NaOH. Has both phenolic and basic properties.

Reactions.—On distillation with zinc-dust it gives flavoline. With acetic anhydride it forms a substance crystallising in needles [128°], which distils undecomposed (O. Fischer a. Rudolph, *B.* 15, 1502). On oxidation with alkaline $KMnO_4$ it is converted successively into lepidine-carboxylic acid, picoline-tri-carboxylic acid, and finally pyridine-tetra-carboxylic acid (O. Fischer a. Täuber, *B.* 17, 2925).

Salts.—$B'HCl^{\times}$: long colourless soluble needles. — $B'_2H_2SO_4{}^{\times}$: colourless needles. — $B'_2H_2Cl_2PtCl_4{}^{\times}$: yellow sparingly soluble needles.

Acetyl derivative $C_{16}H_{12}N(OAc)$: long needles or small plates [128°] (Besthorn a. O. Fischer, *B.* 16, 69).

Pseudo-flavenol $C_{16}H_{13}NO$ *i.e.*



$$C_6H_4\left\langle\begin{array}{l}CH{:}CH\\ \quad\quad |\\ N{=}C.C_6H_3Me.OH\end{array}\right.$$

[196°].

Preparation.—From pseudo-flavaniline by the action of nitrous acid ; oxy-pseudo-flavenol [89°] and nitro-pseudo-flavenol are also formed. It is separated from these by shaking with ether, which extracts the oxy- compound, and then ppg. the impure pseudo-flavenol by CO_2. Crystallised from absolute alcohol.

Properties.—Plates. Sol. hot alcohol, ether, benzene, and chloroform. Oxidised by CrO_3 to quinoline (*Py.* 3)-carboxylic acid [157°]. It is reduced by zinc-dust to the base pseudoflavoline $C_{16}H_{11}N$, ortho-cresol, and quinoline. Tin and HCl convert it into a tetrahydro-compound, which, when fused with potash, is oxidised to α-oxy-iso-phthalic, *p*-oxy-benzoic, and salicylic acids (Weidel a. Bamberger, *M.* 9, 99).

Salts.—$B'HCl\,2aq$: pale yellow needles.—$(B'HCl)_2PtCl_4$: yellow crystalline powder.

Acetyl derivative $C_{16}H_{12}NOAc$: [106°]; plates.

Nitro-pseudo-flavenol $C_{16}H_{12}(NO_2)NO$. [160°].

FLAVINE *v.* Di-amido-benzophenone.

FLAVOÏDINE. A name proposed by Meldola (*C. N.* 50, 267) to denote azo- bases of the form $NH_2R''.N_2.R''NH_2$, isomeric with the chrysoïdines.

FLAVOL *v.* Di-oxy-anthracene.

FLAVOLINE *v.* (*Py.* 3:1)-Phenyl-methyl-quinoline.

FLAVOPURPURIN *v.* Tri-oxy-anthraquinone.

FLAVOQUINOLINE *v.* (*Py.* 1)-Methyl-(*Py.* 3: *B.*3)-diquinoline.

FLUAVIL *v.* Gutta percha.

FLUO-. *Use of this prefix applied to inorganic compounds*: for *fluo-salts v.* the salts to the name of which *fluo-* is prefixed. Thus, *fluo-niobates*, *fluo-silicates*, and *fluo-stannates* will be described under Niobates, Silicates, and Stannates, and these salts will be found under the general headings Niobium, Silicon, and Tin. M. M. P. M.

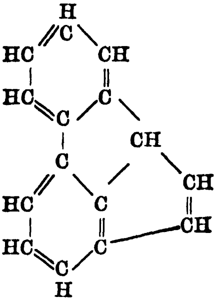
FLUO-BENZENE *v.* Fluoro-benzene.

FLUOBENZOIC ACID *v.* Fluorobenzoic acid.

FLUOBORIC ACID and FLUOBORATES $H_2B_2O_4.6HF$ and $M_2B_2O_4.6HF$ (*v.* vol. i. p. 530).

FLUORANILINE *v.* Fluoro-aniline.

FLUORANTHENE $C_{15}H_{10}$ *i.e.*



(Fittig a. Liepmann, *B.* 12, 164). *Idryl.* [110°]. (251° at 60 mm.). V.D. 6·64 (calc. 6·57).

Occurrence.—In coal-tar (Fittig a. Gebhard, *A.* 193, 142). Found also to the extent of 3 p.c. amongst the solid hydrocarbons obtained in Idria in distilling mercury from its ore (Goldschmiedt a. Schmidt, *M.* 2, 1), and in American petroleum (Prunier, *Bl.* [2] 31, 293).

Preparation.—Crude pyrene from coal-tar is converted into the picric acid compound by treatment with an alcoholic solution of picric acid. The picric acid compound of fluoranthene is more soluble in alcohol than that of pyrene. The hydrocarbon is liberated from this compound by NH_3, and is recrystallised from alcohol. Fluoranthene may also be separated from pyrene by fractional distillation under 60 mm. pressure when pyrene boils 10° higher (Fittig a. Liepmann, *A.* 200, 1).

Properties. — Large colourless monoclinic plates (from dilute alcohol) $a{:}b{:}c = 1{\cdot}495{:}1{:}1{\cdot}025$; $\beta = 82°\ 50'$; or thin needles (from alcohol). Sl. sol. cold, v. sol. hot, alcohol ; v. sol. ether, CS_2, and HOAc. Warm conc. H_2SO_4 dissolves it, forming a blue solution. Its picric acid compound $C_{15}H_{10}C_6H_2(NO_2)_3OH$ [183°] forms long reddish-yellow needles, which may be recrystallised from alcohol without decomposition.

Tri-chloro-fluoranthene $C_{15}H_7Cl_3$. [above 300°]. Needles (Goldschmiedt, *M.* 1, 222).

Di-bromo-fluoranthene $C_{15}H_8Br_2$. [205°]. From fluoranthene in CS_2 and Br (F. a. G.). Light-yellow needles (from CS_2).

Tri-bromo-fluoranthene $C_{15}H_7Br_3$. From fluoranthene in HOAc and Br. Needles. Does not melt below 345° (G.).

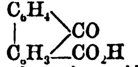
Tri-nitro-fluoranthene $C_{15}H_7(NO_2)_3$. [above 300°]. From fluoranthene and fuming HNO_3. Minute yellow needles. Insol. ordinary solvents, sol. hot HNO_3.

Fluoranthene dihydride $C_{15}H_{12}$. [76°]. From fluoranthene by treatment of its alcoholic solution with sodium amalgam, or by heating with HIAq and red phosphorus at 180° (Goldschmiedt). Needles (from alcohol). Its picric acid compound $C_{15}H_{12}C_6H_2(NO_2)_3OH$ [186°] crystallises from alcohol in red needles.

Fluoranthene octohydride $C_{15}H_{18}$. (311°). From fluoranthene, HIAq, and red phosphorus at 250° (G.).

Fluoranthene disulphonic acid $C_{15}H_8(SO_3H)_2$. From fluoranthene (1 pt.) and H_2SO_4 (2 pts.) at 100° (G.). Unstable syrup. Potash-fusion gives crystalline $C_{30}H_{20}O_8$[246°].—K$_2$A″ aq.—CaA″4aq. —BaA″2½aq: m. sol. water.—CdA″ 2½aq. On distilling the K salt with KCy and fusing the product with KOH there is formed the carboxylic acid $C_{15}H_9CO_2H$ [165°].

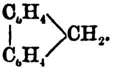
Fluoranthene - quinone $C_{15}H_8O_2$. [189°]. Formed, together with a large proportion of diphenylene ketone carboxylic acid



$$\begin{matrix} C_6H_4 & \diagdown & \\ | & & CO \\ C_6H_3 & \diagup\!\!-\! & CO_2H \end{matrix}$$

by oxidising fluoranthene with chromic acid mixture (F. a. L.). After removing the acid by aqueous Na_2CO_3 alcohol extracts the crystalline compound $C_{15}H_8O_2(C_{15}H_{10})_2$[102°] whence aqueous $NaHSO_3$ extracts the quinone. On addition of HCl to the solution in $NaHSO_3$ there are ppd. nearly colourless needles, apparently consisting of the hydroquinone; these are converted in great part into the quinone during recrystallisation from alcohol, or more quickly by oxidation with $FeCl_3$. Small red needles (from alcohol); m. sol. alcohol and HOAc.

FLUORENE $C_{13}H_{10}$ *i.e.*



$$\begin{matrix} C_6H_4 & \diagdown & \\ | & & CH_2 \\ C_6H_4 & \diagup & \end{matrix}$$

(*a*)-*Diphenylene-methane*. Mol. w. 166. [113°]. (c. 302°) (A.); (295° i. V.) (F. a. S.). V.D. 5·77 (calc. 5·78).

Occurrence.—In the portion of coal-tar boiling between 300° and 400° (Berthelot, *A. Ch.* [4] 12, 222; Barbier, *A. Ch.* [5] 7, 472).

Formation.—1. From diphenylene ketone by distilling with zinc-dust (Fittig, *B.* 6, 187; Fittig a. Schmitz, *A.* 193, 134) or by heating with HIAq and amorphous phosphorus at 160° (Graebe, *B.* 7, 1625).—2. By passing diphenyl-methane through red-hot tubes (Graebe, *A.* 174, 194).—3. From diphenyl and CH_2Cl_2 under the influence of $AlCl_3$ (Adam, *Bl.* [2] 47, 686).—4. By distilling the di-carboxylic acid with lime (Bamberger a. Hooker, *B.* 18, 1036).—5. By distilling phenanthraquinone with lime (Anschütz a. Schultz, *A.* 196, 44).—6. By heating ellagic acid with zinc-dust in a current of hydrogen (Barth a. Goldschmiedt, *B.* 11, 846).

Preparation.—By fractionally distilling the hydrocarbons contained in coal-tar about 20 litres of a portion boiling from 300° to 320° is collected; this is solidified by cold, pressed, and redistilled; a fraction 290° to 310° (10 litres) is then obtained by distillation. After one more distillation the fraction 295° to 305° is recrystallised successively from alcohol-benzene, alcohol, and HOAc (Barbier). Still further purification may be effected by means of the picric acid compound.

Properties.—Very small white plates (by sublimation) exhibiting, when not perfectly pure, violet fluorescence. If recrystallised several times from alcohol and then from glacial acetic acid it is no longer fluorescent (Hodgkinson a. Matthews, *C. J.* 43, 163). V. sol. ether, benzene, CS_2, and hot alcohol, sl. sol. cold alcohol.

Reactions.—1. Boiling with CrO_3 in HOAc forms diphenylene ketone, but no quinone.—2. *Potash-fusion* gives di-oxy-diphenyl [98°] and other products.—3. When its vapour is passed over heated *lead oxide* there are formed two hydrocarbons, $C_{26}H_{14}$ and $C_{26}H_{16}$. The latter forms red trimetric crystals (from HOAc) [183°] (above 360°); gives an unstable picric acid compound [178°]; and is reduced in alcoholic solution by sodium-amalgam to colourless $C_{26}H_{18}$ [242°] (De la Harpe a. Van Dorp, *B.* 8, 1049). The hydrocarbon $C_{26}H_{14}$ forms long yellow needles (from benzene-alcohol) [270°].—4. When fluorene is passed over red-hot MnO_2 a red mass is obtained, and if this be freed from fluorene by heating somewhat above 300° and from the red body by washing with ether, there is left the hydrocarbon $C_{26}H_{18}$ [246°] termed 'para-difluoryl.' It forms long thin prisms, v. sl. sol. cold ether, m. sol. hot HOAc. It decomposes above 250°. It forms a tetra-bromo- derivative [302°], and is oxidised by CrO_3 in HOAc to $C_{26}H_{14}O_2$ [255°]. Two other hydrocarbons, $C_{26}H_{18}$, appear to accompany the one described [246°] in the red mass (Hodgkinson, *C. J. Proc.* 1, 36).—5. Conc. HIAq (40 pts.) at 275° forms $C_{13}H_{28}$ (240°), hexane and heptane being also formed according to Berthelot (*A. Ch.* [5] 7, 510).—6. On adding the calculated quantity of *bromine* dissolved in CS_2 to a solution of fluorene in CS_2 dibromo-fluorene $C_{13}H_8Br_2$ [167°] is formed. It crystallises from CS_2 in monoclinic forms. By treatment with more Br in the cold there is produced the tri-bromo-fluorene $C_{13}H_7Br_3$ [162°] (*v.* DI-BROMO-FLUORENE). Bromine vapour passed into a cold solution of fluorene in CS_2 forms light-yellow needles of $C_{13}H_9Br_3$ which is quickly converted by alcoholic KOH into di-bromo-fluorene. By the simultaneous action of bromine and KOH on fluorene there is formed a bromo-fluorene [104°] (Hodgkinson, *C. J. Proc.* 1, 36).—7. *Chlorine* passed into a solution of fluorene in CS_2 forms $C_{13}H_8Cl_2$ [118°] and $C_{13}H_7Cl_3$ [147°] (*v.* DI-CHLORO-FLUORENE).—8. A mixture of fuming *nitric acid* and HOAc forms nitro-fluorene $C_{13}H_9(NO_2)$ [154°] and di-nitro-fluorene $C_{13}H_8(NO_2)_2$ [201°] (*v.* NITRO-FLUORENE). The former may be reduced by tin and HCl to *p*-amido-fluorene [125°], which crystallises in needles and forms an acetyl derivative [188°] (Strasburger, *B.* 17, 108). Di-amido-fluorene $C_{13}H_8(NH_2)_2$ [157°] is obtained by distilling di-amido-diphenic acid with lime; its acetyl derivative [250°] crystallises in leaflets (Schultz, *A.* 203, 99).—9. Treated with phenyl-acetic chloride and $AlCl_3$ it gives the ketone $C_{13}H_9.CO.CH_2.C_6H_5$ [156°] which crystallises in small tables, sl. sol. cold alcohol and ether (Päpcke, *B.* 21, 1341). This ketone is converted by benzyl chloride and NaOEt into $C_{13}H_9.CO.CHPh.CH_2C_6H_5$ [150°] which crystallises from alcohol in slender needles.

Picric acid compound $C_{13}H_{10}C_6H_2(NO_2)_3OH$. [82°]. Obtained by adding picric acid to an ethereal solution of the hydrocarbon. Reddish-brown prisms. Decomposed by boiling with water or alcohol.

Picryl chloride compound $C_{13}H_{10}C_6H_2(NO_2)_3Cl$. [70°]. Orange needles (Liebermann a. Palm, *B.* 8, 377).

Fluorene sulphonic acid $C_{13}H_9SO_3H$. From fluorene in $CHCl_3$ and $ClSO_3H$ (Hodgkinson a. Matthews, *C. J.* 43, 166). Gummy. V. sol.

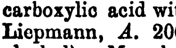
water. Fused with KOH at a little above 400° it forms two tri-oxy-diphenyls (*q. v.*), for not only is SO_3H displaced by OH but CH_2 is displaced by 2(OH).

Salts.—KA′: minute cubes.—$BaA'_2$2aq.—$CdA'_2$6aq.

Isomeride of fluorene. — DI-PHENYLENE-METHANE.

FLUORENE ALCOHOL *v.* DI-PHENYLENE CARBINOL.

FLUORENE CARBOXYLIC ACID



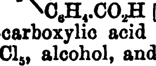
$$CH_2\left<\begin{matrix}C_6H_4\\ |\\ C_6H_3.CO_2H\end{matrix}\right.$$

[3:2:1]. *Fluorenic acid.* [246°]. Formed by reducing diphenylene ketone carboxylic acid with sodium-amalgam (Fittig a. Liepmann, *A.* 200, 13). Small crystals (from alcohol). May be sublimed. Sl. sol. boiling water, v. sol. hot alcohol. Gives fluorene when distilled with lime. Alkaline permanganate oxidises it to diphenylene ketone carboxylic acid.

Salts.—BaA'_2 3aq: glittering scales, sl. sol. water.—CaA'_2 2½aq: hard white needles.

Ethyl ether EtA′. [54°]. Colourless prisms, v. sol. hot alcohol.

Fluorene carboxylic acid



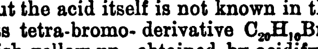
$$CH_2\left<\begin{matrix}C_6H_4\\ |\\ C_6H_4.CO_2H\end{matrix}\right.$$

[2:3:1]. [175°]. From diphenyl *o*-carboxylic acid by successive treatment with PCl_5, alcohol, and zinc and HOAc (Graebe a. Aubin, *A.* 247, 257). V. sol. alcohol, ether, and HOAc.

Methyl ether MeA′. [64°].

Fluorene-di-carboxylic acid $C_{13}H_8(CO_2H)_2$. Formed by reduction of diphenylene-ketone-di-carboxylic acid with sodium-amalgam in the cold, sl. sol. alcohol, ether, and HOAc. On distillation with lime it gives fluorene (Bamberger a. Hooker, *B.* 18, 1036; *A.* 229, 161).—Ag_2A''.

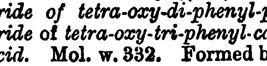
FLUORESCEÏC ACID $C_{20}H_{14}O_6$ *i.e.*



$$CO_2H.C_6H_4.C(OH)\left<\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}\right>O.$$

Fluoresceïn may be looked upon as the anhydride of this acid; but the acid itself is not known in the free state. Its tetra-bromo- derivative $C_{20}H_{10}Br_4O_6$ is a reddish-yellow pp., obtained by acidifying the product of the action of conc. aqueous KOH upon eosin. Its di-nitro- derivative is obtained in like manner from di-nitro-fluoresceïn, and forms red crystals (from alcohol).

FLUORESCEIN $C_{20}H_{12}O_5$ *i.e.*

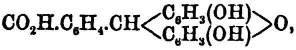


$$CO\left<\begin{matrix}C_6H_4\\ O\end{matrix}\right>C\left<\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}\right>O$$

[1:4:6]. *Anhydride of tetra-oxy-di-phenyl-phthalide. Anhydride of tetra-oxy-tri-phenyl-carbinol carboxylic acid.* Mol. w. 332. Formed by heating phthalic anhydride (5 pts.) with resorcin (7 pts.) at 200°, until the mass gets viscid; the product is boiled with water, washed with alcohol, dissolved in aqueous alkali, and ppd. as a yellow powder by an acid (Baeyer, *B.* 4, 658; *A.* 183, 1). According to Mulhäuser (*D. P. J.* 263, 49) phthalic anhydride (17½ kilos.) is added with stirring to melted resorcin (25 kilos.), and after heating for 1½ hours at 180° the reaction begins, and lasts for 40 minutes. Resorcin and di-oxy-toluene $C_6H_3(OH)_2Me$[1:3:4] give with phthalic anhydride fluorescent derivatives, while orcin, $C_6H_3(OH)_2Me$[1:3:5] does not. Hence, to form a fluorescent body the phthalic acid residue must probably go into the position 5.

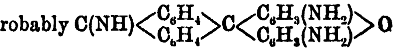
Properties.—Dark-red prisms (from alcohol). Sl. sol. hot water, more sol. dilute acids. When freshly ppd. it is v. sol. alcohol and ether, but in the crystallised state it dissolves only on boiling. V. sol. hot HOAc, nearly insol. benzene and chloroform. The ethereal solution is pale-yellow, and not fluorescent; the alcoholic solution exhibits green fluorescence. Fluoresceïn dissolves readily in aqueous alkalis, the solution exhibiting when dilute a splendid yellowish-green fluorescence. It also dissolves in alkaline carbonates, baryta, and lime-water. Fluoresceïn begins to decompose at 290°. It dyes silk and wool yellow; but it has little tinctorial value, although it is the starting-point for the eosin colouring matters, which are derived from it by displacement of hydrogen by Br, I, NO_2, &c. On adding alcoholic NH_3 to an ethereal solution of fluorescein a reddish-yellow pp. is formed, which, however, loses NH_3 on drying.

Reactions.—1. Boiling with aqueous NaOH and zinc-dust decolourises it. On adding an acid and shaking with ether fluorescin $C_{20}H_{14}O_5$, or



$$CO_2H.C_6H_4.CH\left<\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}\right>O,$$

is dissolved; on evaporation it is left as a varnish. Its alkaline solution is readily reoxidised to fluoresceïn.—2. Fusion with caustic NaOH forms resorcin and the acid $C_{14}H_{10}O_5$ or $CO_2H.C_6H_4.CO.C_6H_3(OH)_2$ [200°], which on further fusion splits up into CO_2, resorcin, and benzoic acid.—3. Conc. H_2SO_4 forms a compound $C_{20}H_{12}O_5SO_3$ [140°-150°], which is resolved by warm water into its components.—4. Boiling with H_2SO_4 for some time forms resorcin-cœrulin, which is ppd. by water in dark-red flakes, and dissolves in alkalis, forming a greenish-blue solution.—5. *Bromine*, in HOAc, forms di-bromo-fluorescein $C_{20}H_{10}Br_2O_5$ [260°-270°] and eosin $C_{20}H_8Br_4O_5$.—6. Aqueous NH_3 when heated with it for 8 hours forms thick orange monoclinic prisms and tables of $C_{20}H_{15}N_3O_2$ which is a direct yellow dye for wool. It is probably



$$C(NH)\left<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\right>C\left<\begin{matrix}C_6H_3(NH_2)\\ C_6H_3(NH_2)\end{matrix}\right>O$$

(R. Meyer a. Oppelt, *B.* 21, 3376).

Metallic derivatives $CaC_{20}H_{10}O_5$4aq. Obtained by boiling fluoresceïn with water and $CaCO_3$ (Schreder, *B.* 11, 1342). Slender reddish-brown needles with green lustre.—$BaC_{20}H_{10}O_5$ 9aq: crimson plates.

Acetyl derivative $C_{20}H_{10}Ac_2O_5$. [200°]. Needles (from alcohol-acetic acid). Sl. sol. alcohol, v. sol. HOAc, insol. ether, benzene, and chloroform.

Benzoyl derivative $C_{20}H_{10}Bz_2O_5$. [215°]. Crystals (from acetone); sl. sol. alcohol and ether.

Ethyl derivative $C_{20}H_{11}EtO_5$. [156°]. From fluorescein, KOH, and alcoholic EtBr at 120°. Pale-yellow needles (from ether); v. sol. alcohol, chloroform, and benzene; insol. dilute alkalis.

Di-ethyl derivative $C_{20}H_{10}Et_2O_5$. Not formed by the action of EtBr on potassium fluorescein, but sparingly formed by the action of EtI on the silver derivative. Pale-yellow plates (from alcohol); sl. sol. ether and alcohol; the alcoholic solution shows a vivid yellow fluorescence. Not dissolved by dilute alkalis, but split up into alcohol and fluoresceïn by conc. KOHAq or H_2SO_4.

Chloride $C_{20}H_{10}O_3Cl_2$. [252°]. From fluoresceïn (1 mol.) and PCl_5 (2 mols.) at 100°. Prisms (from toluene-alcohol). V. sol. hot benzene and toluene, sl. sol. alcohol and ether. Not affected by aqueous or alcoholic KOH, but destroyed by potash-fusion. Water and slaked lime at 230° reconvert it into fluoresceïn. Reduced in alcoholic solution by NaOH and zinc-dust to $C_{20}H_{12}Cl_2O_3$ [226°]. Sol. alcohol, benzene, ether, and acetone (Drewsen, *A.* 212, 351). Fuming HIAq at 150° gives $C_{20}H_{12}O_4I_2$, which crystallises from alcohol in plates [230°]. Sol. dilute, but insol. conc., KOHAq.

References.—Di-bromo-, Di-bromo-di-nitro-, Chloro-, Di-chloro-tetra-iodo-, and nitro-fluoresceïn.

Homofluoresceïn (so-called) $C_{23}H_{18}O_5$. Prepared by the action of chloroform and NaOH on orcin (Schwarz, *B.* 13, 543). Red, metallic-green needles or plates. Sl. sol. water, alcohol, and cold acetic acid, insol. ether, benzene, and ligroïn. Its dilute alkaline solutions have a strong green fluorescence. It is a weak dibasic acid. The sodium salt forms fine yellowish-red needles, sol. water; the barium salt red needles or scales, and the silver salt a dark-red powder. Its substitution-products dye wool and silk various shades of yellow and red.

Tetra-acetyl derivative $C_{23}H_{14}O(OAc)_4 + 2H_2O$? Amorphous powder or brownish-yellow plates. Insol. water, sol. alcohol.

Tetra-bromo-homo-fluoresceïn $C_{23}H_{14}Br_4O_5$. Brown leaflets. Sol. alcohol.—$NaC_{23}H_{13}Br_4O_5$ 4aq: microscopic red needles, sol. NaOHAq.

Tri-iodo-homofluoresceïn $C_{23}H_{15}I_3O_5$. Microscopic red crystals.—$NaC_{23}H_{14}O_5I_3$. Red microscopic needles, sol. hot water and dilute alcohol, insol. NaOHAq.

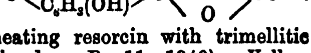
Hexa-nitro-oxy-homofluoresceïn $C_{21}H_{12}(NO_2)_6O_6$ aq. Reddish-yellow leaflets. Formed by nitration of homofluorescein. By boiling with aqueous NH_3 it forms the acid $C_{23}H_{14}N_8O_{16}$, and by the action of KCN the acid $C_{25}H_{14}N_8O_{17}$. The nitrate is a yellowish-red crystalline powder, explodes at 180°, sol. alcohol.—A′Na and A′Ag. Small red leaflets.

Hexa-amido-oxy-homofluoresceïn $C_{23}H_{12}(NH_2)_6O_8$. Colourless microscopic crystals. Produced by reduction of the hexa-nitro- compound.

Hexa-nitro-homofluoresceïn-cyamic acid $C_{25}H_{14}N_8O_{17}$ aq. Crystalline powder. Sparingly sol. water and alcohol. Formed by the action of KCN on the hexa-nitro- compound.—$A''K_2$. Fine yellow soluble needles.

Compound $C_{23}H_{14}N_8O_{16}$. Reddish-yellow powder. Formed by boiling the nitrate of the hexa-nitro- compound with aqueous NH_3.—$A''(NH_4)_2$. Reddish-yellow scales or small yellow needles (Schwarz, *B.* 13, 543).

FLUORESCEÏN CARBOXYLIC ACID

$C_{21}H_{12}O_7$ *i.e.* 

$$O\left<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}\right>C\left<\begin{matrix}C_6H_3—CO_2H\\ \quad\ \ \ >CO\\O\end{matrix}\right.$$

Prepared by heating resorcin with trimellitic anhydride (Schreder, *B.* 11, 1340). Yellow amorphous powder; v. sl. sol. water and HOAc, v. sol. alcohol, ether, and benzene. The metallic derivatives $Ba_3A'''_2$ and $Ca_3A'''_2$ are red amorphous powders.

Acetyl derivative $C_{21}H_{10}Ac_2O_7$: yellow flocculi.

Di-bromo- derivative $C_{21}H_{10}Br_2O_7$: red needles.

Tetra-bromo- derivative $C_{21}H_8Br_4O_7$: red amorphous powder.—$K_3C_{21}H_5Br_4O_7$.

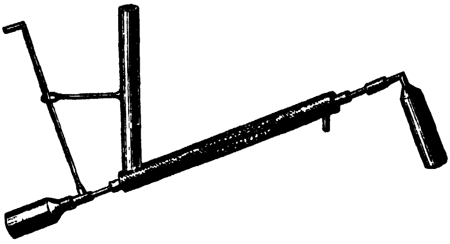
FLUORESCEÏN-SULPHONIC ACID $C_{20}H_{11}O_5(SO_3H)$. Reddish-yellow needles or prisms. Easily soluble in alcohol and hot water, less readily in cold water, insoluble in ether. Its aqueous solution is yellow, with a slight fluorescence; the alkaline solution possesses a powerful green fluorescence. Obtained by heating (β)-sulphophthalic acid with resorcin.—A'''_2Ca_3. Red solid, very soluble in alcohol (Graebe, *B.* 18, 1129).

FLUORHYDRIC ACID. HF. (*Hydrofluoric acid. Hydrogen fluoride.*) Mol. w. 20. [−92·3°] (Olszewski, *M.* 7, 371). (19·44°) (Gore, *Pr.* 17, 256). S.G. $\frac{12\cdot78°}{12\cdot78°}$ ·9879 (Gore, *l.c.*). V.D. c. 10 at 100° (Gore, *Fr.* 1869. 173); 19·6 at 30·5° (Mallet, *Am.* 3, 189); 25·6 at 26·4°, 10·3 at 88·3° (Thorpe a. Hambly, *C. J. Trans.* 1888. 765; 1889. 163). Vapour pressure at 15° = 394 mm. (Gore).

Schwankhardt observed in 1670 that glass could be etched by fluorspar and sulphuric acid; Scheele, in 1771, recognised that this etching was due to the formation of an acid from the fluorspar; Wenzel prepared the acid fairly pure; Gay-Lussac and Thénard, in 1810, examined its properties; and Ampère suggested that the acid was not an oxygen compound. Gore, in 1868, obtained the pure acid.

Formation.—1. By decomposing calcium fluoride (*fluorspar*) by sulphuric acid.—2. By heating acid potassium fluoride, KHF_2.—3. By the reaction of dry H_2S with PbF_2.—4. By heating AgF in a stream of H.

Preparation.—1. 200 grams dry KHF_2 are heated in a Pt retort so long as moisture comes off; the neck of the retort is then connected with a small condenser made of Pt, the joint being made tight by molten sulphur; this condenser is filled with a freezing mixture, more of which can be supplied by a specially arranged charging apparatus; the condenser ends in a small Pt flask, from the neck of which a long Pt tube passes upwards. On continued heating the KHF_2 is decomposed to KF + HF; the HF is condensed and received in the Pt flask; the air in the apparatus escapes through the Pt tube, the length of which prevents the entrance of moisture. The figure shows the arrangement.—2. Approximately pure liquid HF may be prepared by gently heating a mixture of pure conc. H_2SO_4 with so much powdered CaF_2 (free from silica) that the whole



remains quite liquid, in a Pt retort connected with a small Pt flask or U tube surrounded by a freezing mixture.—3. An aqueous solution of HF is prepared by heating together powdered CaF_2 and conc. H_2SO_4 in a leaden retort, and leading the gas into water in a vessel of Pt or Pb kept cold by ice (for description of the apparatus *v.* Brieglieb, *A.* 111, 380). Commercial HFAq may be purified by passing H_2S into it, adding enough K_2CO_3 to saturate the H_2SO_4 and H_2SiF_6 present, decanting from the pp., removing H_2S by $AgCO_3$, filtering and distilling from a retort of Pb or Pt (Gore, *l.c.*). The aqueous acid is kept in bottles made of gutta percha.

Properties.—A colourless, very mobile liquid, which fumes in the air and absorbs water very rapidly. Burns and inflames if let fall on the skin. The vapour is very irritating and very poisonous. The anhydrous acid should be kept in Pt flasks with tight-fitting Pt caps covered with paraffin. Solidifies at $-102{\cdot}5°$ and liquefies again at $-92{\cdot}3°$ (Olszewski, *M.* 7, 371). A conc. aqueous solution of HF is a colourless, strongly acid liquid, which fumes in the air; when distilled at 760 mm. HF is evolved and a liquid remains, containing 36-38 p.c. HF; when this acid is kept in contact with chalk for a little the liquid then contains 32·5-32·7 p.c. HF; when dilute HFAq is distilled at 760 mm. water is evolved until the liquid contains 32·2-32·4 p.c. HF, when the composition remains constant (Roscoe, *C. J.* 13, 162). S.G. of HFAq 35·9 p.c. HF = 1·15; S.G. of most conc. HFAq = 1·06. Bineau regarded the acid of 35·9 p.c. as a hydrate $HF.2H_2O$, but Roscoe's observations, which show that composition varies with pressure, render the existence of a definite hydrate improbable. When HFAq is neutralised by soda much heat is produced; [HFAq,NaOHAq] = 16,272 (*Th.* 1, 157). Addition of HFAq to the NaF thus formed causes disappearance of heat [NaFAq,HFAq] = −288 (Thomsen). The heat of neutralisation of HFAq is 18 to 19 p.c. greater than that of the analogous haloid acids; HF is the only haloid acid the reaction of which with its own alkali salts is attended by the disappearance of a considerable quantity of heat. The *relative affinity* of HFAq is extremely small, being less than 1 if that of HClAq is taken as 100 (*cf.* AFFINITY, vol. i. p. 75).

Molecular weight.—If HF is the molecular formula of fluorhydric acid the vapour density of the compound must be 10 (H = 1); Gore determined the V.D. indirectly by heating a known volume of H with a slight excess of AgF and measuring the HF produced; at 100° the volume of HF was approximately double that of the H, but at lower temperatures it was considerably less (*Tr.* 1869. 173). Mallet weighed the HF gas in a flask coated internally with paraffin; at 30·5° the V.D. was found to be 19·6, which corresponds fairly well with the formula H_2F_2 (*Am.* 3, 189). Thorpe and Hambly (*C. J. Trans.* 1888. 765; 1889. 163) have determined the V.D. of HF in a specially constructed apparatus of Pt; they made 14 experiments at temperatures between 26·4° and 88·3°; the V.D. varied from 25·6 at 26·4° to 10·3 at 88·3°; these results rather point to the gradual breaking down of a complex molecular group as temperature rises, with final production of molecules of HF, than to the existence of definite molecules of H_2F_2 at one temperature and HF at another. They have also examined the effect of altering pressure, at constant temperature, on the V.D. of HF. The temperature chosen was 32°, because the V.D. at this temperature and 760 mm. pressure corresponds with the formula H_2F_2. A small lowering of pressure was accompanied by considerable decrease of V.D.; hence there is no evidence of the existence of a stable gaseous molecule H_2F_2. Nevertheless the results do not negative the view that the composition of the chemically-reacting unit of fluorhydric acid is represented by the formula H_2F_2. This view is in keeping with the readiness with which fluorides such as KFHF(= KHF_2) are produced (*v.* FLUORIDES). But it might be argued that the existence of the salts KF.2HF and KF.3HF (Moissan, *C. R.* 106, 547) points to the existence of the acids H_3F_3 and H_4F_4.

Reactions.—1. When dilute HFAq is *electrolysed* in a Pt vessel, H and O (with ozone) only are evolved; if the solution contains 80 p.c. HF the acid is decomposed, H is evolved at the kathode, and the anode is attacked by the F there produced (Gore, *Pr.* 17, 256). Electrolysis of liquid HF kept at −23° results in production of fluorine at the anode (Moissan, *C. R.* 103, 202, 256); for details of apparatus, &c. *v.* FLUORINE, p. 461.—2. *Liquid hydrofluoric acid* at −29° to −18° does not react with *non-metals*, nor with *metals* except the *alkali metals*; it reacts violently with many *anhydrides*, *e.g.* P_2O_5, SO_3; *chlorides of alkali and alkaline earth metals* are decomposed, also *chlorides of phosphorus, antimony, and titanium*; many *organic bodies* are rapidly charred; *paraffin* is unchanged; *glass* is unattacked by perfectly dry liquid HF, but if a trace of moisture is present SiF_4 is formed (for other similar observations *v.* Gore, *Pr.* 17, 256; *Tr.* 1869. 173).—3. An *aqueous solution of hydrofluoric acid* reacts with *metals* and *metallic oxides* very similarly to HClAq, forming fluorides, and evolving H with metals, and forming water with metallic oxides; *silicon*, *boron*, *tantalum*, and *zirconium*, are dissolved by HFAq.—4. *Silica* and *silicates* are rapidly decomposed by HFAq with evolution of gaseous SiF_4; if water is present in considerable quantity the SiF_4 reacts with it to produce silicofluorhydric acid H_2SiF_6 (*v.* SILICO-FLUORIDES under SILICON). This reaction is made use of in etching glass.—5. *Titanic*, *tin*, *tantalic*, *molybdic*, and *tungstic oxides*, which are insoluble in most acids, are dissolved by HFAq forming fluorides, which then combine with HF (*v.* TITANO-FLUORIDES, STANNO-FLUORIDES, &c., under TITANIUM, TIN, &c.).—6. With *metallic oxides* HFAq reacts to form fluorides, and in many cases these combine with xHF (*v.* FLUORIDES).

Combinations.—With many *fluorides* to form salts, of which KF.HF, $NH_4F.HF$, $BiF_3.3HF$, and $SiF_4.2HF$, are typical. Certain of these compounds of HF with fluorides are best regarded as distinct acids, *e.g.* $SiF_4.2HF$ reacts as an acid, forming salts, $M^I_2SiF_6$, known as *silico-fluorides*; *stanno-fluorides*, *tantalo-fluorides*, &c., are also known; these salts are described under their respective headings as sections of the articles SILICON, TIN, TANTALUM, &c. (*v. also* FLUORIDES).

M. M. P. M.

FLUORIDES. *Binary compounds of F with other elements.* Fluorides of all the metals with the exception of 10 or 12 (and these mostly rare metals which have not been at all thoroughly examined) have been prepared. Fluorides of the following non-metals are also known, viz. B, H, I, P, Se, S, and Te; no fluoride of Br, C, Cl, N, or O has yet been isolated. Fluorides are prepared (1) by the reaction between HFAq and metals or metallic oxides; (2) by heating fluorspar and H_2SO_4 with metallic oxides, this method is applicable to volatile metallic fluorides; (3) by ppn., applicable to insoluble metallic fluorides; (4) by heating non-metals with HgF_2 or PbF_2. Metallic fluorides are generally easily fusible solids, similar to, and, as a rule, isomorphous with, the chlorides. Some non-metallic fluorides are gaseous at ordinary temperatures, *e.g.* SiF_4 and PF_5; others are liquids, *e.g.* IF_5; and a few are solids, *e.g.* SbF_3. Metallic fluorides are generally insoluble in water; AgF and SnF_2 are soluble, and FeF_3, NaF, and KF, are sparingly soluble. The fluorides of Bi and Sb are not decomposed by water, whereas the chlorides of these metals are at once decomposed. Most metallic fluorides are very stable, not being decomposed either by heat, or by heating with carbon or in oxygen; solutions of these fluorides generally react slowly with alkaline silicates forming HF and basic fluorides. Non-metallic fluorides are generally more stable than the corresponding bromides, chlorides, or iodides; thus PCl_5 is dissociated by heat, but PF_5 is an extremely stable gas. Fluorides are decomposed by heating with Cl or with conc. H_2SO_4. Almost all metallic fluorides readily combine with HF forming acid salts, aqueous solutions of which turn blue litmus red and etch glass; these acid salts are decomposed by heat with evolution of HF. Some of these acid salts are better regarded as distinct acids, the negative radicle of which is formed of metal and fluorine; the following probably belong to this class: $SnF_4.2HF$, $TiF_4.2HF$, $ZnF_4.2HF$; $(=H_2MF_6)$. Fluorides, as a class, combine together to form double fluorides; the fluorides of the alkali metals show a remarkable readiness to combine with other metallic fluorides; in many cases, but not in all, as many molecules of alkali fluoride combine, as there are atoms of fluorine in the other fluoride, *e.g.* $BeF_2.2NaF$, $BiF_3.3KF$. These double fluorides are generally more stable compounds than corresponding double chlorides, bromides, or iodides. The readiness with which acid fluorides and double fluorides are produced has suggested that the formula expressing the composition of what may be called the *chemical molecule* of fluorhydric acid should be written H_2F_2. This is perhaps confirmed by the especial ease with which alkali fluorides form acid fluorides MHF_2; thus KF and NaF react with an acid so weak as acetic to form KHF_2 and $NaHF_2$ respectively ($2KFAq + C_2H_4O_2Aq = KF.HFAq + C_2H_3KO_2Aq$). The fact that the quantity of heat which disappears when HFAq reacts with NaF amounts to about 2 p.c. of the heat of neutralisation of HF by NaOH, whereas when the other haloid acids react with their alkali salts hardly any heat disappears, tends to confirm the view that the reacting unit of fluorhydric acid is H_2F_2 rather than HF. The very small affinity of HFAq (less than 1 when that of HClAq = 100), especially taken in conjunction with the marked stability of the fluorides, also marks off this acid from the other haloid acids.

Fluorides are detected by gently heating with conc. H_2SO_4 in a leaden or platinum vessel, which is covered with a piece of glass coated with wax, through which lines are traced with a needle; after a little the glass is removed and the wax wiped off when warm; the glass appears etched where it was exposed to the vapour of HF coming from the fluoride. Fluorides may also be detected by mixing with microcosmic salt and heating strongly by a small blowpipe flame in a glass tube open at both ends; HF is evolved and partially condenses with water on the upper parts of the tube; on evaporating the water a dull spot is seen on the glass.

Fluorides are estimated by evaporation with conc. H_2SO_4, the residual metallic sulphate is weighed, and the fluorine is determined by difference. Or the issuing vapour is led into water, a weighed quantity of PbO is added, the whole is evaporated to dryness and heated, and the residue is weighed; in this process F is substituted for O; if d = increase in the weight of the oxide of lead used, then

$$\text{amount of F in residue} = \frac{19}{19-8}d.$$

For details, and also for other methods of estimating F and HF in presence of fluorides, and for separation of F from other elements, a manual of analysis must be consulted. M. M. P. M.

FLUORINE. F. At. w. 19. Mol. w. 38 (Moissan, *C. R.* 109, 861). For chief lines in emission-spectrum, *v.* Salet (*A. Ch.* [4] 28, 34) and Moissan (*C. R.* 109, 937).

History.—Schwankhardt, in Nürnberg, observed in 1670 that glass is etched by contact with sulphuric acid and fluorspar. About 110 years after this, Scheele showed that the etching observed by Schwankhardt was due to a distinctive acid produced by the reaction between the fluorspar and sulphuric acid. Gay-Lussac and Thénard obtained this acid in 1808 (*A. Ch.* 69, 204), and endeavoured, unsuccessfully, to demonstrate the presence of oxygen in it. In 1810 Ampère declared the acid to be analogous to hydrochloric acid, and to be a compound of H with an element resembling chlorine. To this element he gave the name of *Phtor* (φθόριος = destroying); but the name *fluorine* was generally employed inasmuch as it suggested that the etching compound of the element was obtained from fluorspar (*spathum fluoricum*). The investigations of Fremy (*A. Ch.* [3] 47, 5) and Gore (*Pr.* 17, 256; *Tr.* 1869. 173) rendered certain the composition of the acid first obtained by Gay-Lussac and Thénard. Davy, in 1809 and 1813 (*Tr.* 1809; 1813. 263) endeavoured to isolate fluorine by leading Cl over heated AgF; as he obtained a gas which seemed to be O he concluded that F had probably been liberated, but had reacted with the glass. He then used Pt vessels, but obtained fluoride of Pt; a trial with vessels of fluorspar was unsuccessful. Baudrimont (*J. pr.* 7, 447) heated a mixture of fluorspar, MnO_2, and H_2SO_4 in a glass vessel, and obtained what he declared to be a mixture of HF, SiF_4, and F; he described F as a yellowish gas which bleached, did not act on glass, and combined with gold; the gas was probably Cl derived from chlorides in the fluorspar used. Knox attempted to decompose HgF by Cl in a vessel of fluorspar (*J. pr.* 9, 118); he obtained HgCl and a yellowish gas which rapidly acted on glass. S. J. Knox electrolysed HF and PbF_2, and obtained a colourless gas, which did not act on Au or Pt (*J. pr.* 20, 172). Louyet (*Ph. C.* 1847. 321) again attempted to decompose HgF by Cl, using a vessel of fluorspar. He obtained a colourless gas which did not attack glass, decomposed water at the ordinary temperature, and combined directly with all metals except Au and Pt. Kämmerer (*J. pr.* 85, 457) allowed I to react with AgF in a vacuous glass tube at 70°-80°; he obtained a colourless gas, which was wholly absorbed by KOHAq, but did not combine with Hg. Phipson (*J. pr.* 88, 63) thought he had isolated F by the reaction between CaF_2, $KMnO_4$, and H_2SO_4; he described it as a colourless gas, which bleached, decomposed water rapidly, and was without action on glass. Prat (*C. R.* 64, 345, 511) decomposed KF by heating with MnO_2 and KNO_3; he treated the gas obtained with baryta, and described the residual gas as F; it was colourless, combined with most metals, also with B and Si, but not with SiO_2. Cillis repeated Prat's experiments, but obtained only O (*Z.* [2] 4, 660). Renisch (*N. J. P.* 12, 1) obtained what he regarded as a mixture of O and F by heating cryolite with PbO_2 and $K_2S_2O_7$. Gore attempted to prepare F by decomposing AgF by Cl (*C. J.* [2] 7, 368). Varenne noticed the production of a gas which attacked Pt by heating $(NH_4)_2Cr_2O_7$ with HF (*C. R.* 91, 989). O. Löw (*B.* 14, 1144, 2440) thought that the greenish gas obtained by breaking up fluorspar from Wösendorf was F; he traced the F to the presence of a fluoride of Ce, which was decomposed with evolution of F. Brauner in 1881 (*B.* 14, 1944) obtained a gas more or less resembling Cl by heating CeF_4, and also by heating PbF_4. In 1886 Moissan electrolysed dry liquid HF in a Pt tube by means of a powerful battery (*C. R.* 102, 1543); H was obtained at the negative pole, and at the positive pole a gas was formed which decomposed water with production of ozone, and was wholly absorbed by Hg with formation of HgF_2; the gas combined energetically with P and Si. A little later (*C. R.* 103, 202, 256) Moissan repeated the electrolysis of HF and obtained F.

Preparation.—The apparatus used by Moissan consists of a U-tube of Pt, with stopper of fluorspar and Pt delivery tubes; the positive electrode is formed of an alloy of Pt with 10 p.c. of Ir; KHF_2 is dried at 100°, and then *in vacuo* over H_2SO_4 and KOH; the salt is then heated in a Pt retort, and the HF is condensed in a Pt receiver surrounded by a freezing mixture. The HF is placed in the U-tube which is surrounded by CH_3Cl boiling at −23°; the current from 20 Bunsen cells, coupled in series, is passed through the liquid; any traces of water in the HF are decomposed with formation of gases at the positive pole; when the HF is perfectly dry electrolysis stops, a little perfectly dry KHF_2 is dissolved in the HF, and the conductivity is thus increased. H is now evolved at the negative pole, while at the positive pole there is produced a colourless gas in which Si, B, As, Sb, S, and I take fire, and which decomposes H_2O, forming HF and ozone, and possesses other distinctive properties quite different from those belonging to a mixture of HF and ozone (*v. Properties and Reactions*).

To determine whether this gas was really F or a perfluoride of H, Moissan connected the electrolytic apparatus with a Pt tube containing KF, to remove traces of HF, and then connected this tube with another made of Pt containing a weighed quantity of iron wire, and attached to an apparatus for collecting any gas which might come from the tube. The whole apparatus was filled with dry CO_2, and an arrangement was adopted for collecting and measuring the H evolved at the negative pole. The tube containing the iron wire was heated to dull redness, the U-tube was cooled to −50°, and electrolysis was begun. The weight of iron fluoride formed was exactly equivalent to that of H evolved; no gas, except a trace of air, was obtained from the tube in which the iron wire was heated. Hence the gas evolved at the positive pole was fluorine. Moissan says that as much as 1·5-2 litres F can be obtained in an hour by this method. He also states that the gas is formed by electrolysis of fused KHF_2.

Properties and Reactions.—Fluorine is a pale yellow-green gas. It decomposes *water*, forming ozone and HF. Crystallised *silicon*, *boron*, *arsenic*, *antimony*, *sulphur*, and *iodine*, take fire at once in the gas. It attacks *metals* less readily, probably because a film of fluoride is soon formed on the surface. *Powdered iron* and *manganese* burn brilliantly in F, when gently heated. *Organic compounds* are rapidly decomposed, alcohol, ether, benzene, &c., take fire at once in the gas. F combines violently with *hydrogen* even in the dark.

Fluorine is allied to Cl, Br, and I; the analogy is shown in the composition and properties of its compounds, but there are points of difference (*v.* FLUORHYDRIC ACID and FLUORIDES).

The atomic weight of fluorine has been determined (1) from determination of V.D., and analyses, of HF (Gore, *Pr.* 17, 256; *Tr.* 1869. 173; Mallet, *Am.* 3, 189; Thorpe a. Hambly, *C. J. Trans.* 1888. 765; 1889. 163); (2) by converting CaF_2 into $CaSO_4$ (Louyet, *A. Ch.* [3] 25, 295; Dumas, *A. Ch.* [3] 55, 170; De Luca, *C. R.* 51, 299); (3) by converting NaF to Na_2SO_4, KF to K_2SO_4, and PbF_2 to $PbSO_4$ (Louyet, *l.c.*; Dumas, *l.c.*); (4) by treating $Mn_2F_6.4NH_4F$ with HCl and KI, and estimating the I set free by titration with $Na_2S_2O_3$ (Christensen, *J. pr.* [2] 34, 41). M. M. P. M.

***m*-FLUORO-ANILINE** $C_6H_4FNH_2$ [1:3]. From $C_6H_4(NHAc).N_2.NC_5H_{10}$ and conc. HF (Wallach, *A.* 235, 266). Oil.—$(B'HCl)_2PtCl_4$.

***p*-Fluoro-aniline** $C_6H_4F.NH_2$ [1:4]. (c. 189°). S.G. $\frac{25}{}$ 1·153. From *p*-fluoro-nitro-benzene, $SnCl_2$, and HCl (Wallach, *A.* 235, 267). Liquid which solidifies in a bath of ether solid and CO_2.

Salts.—$B'HCl$.—$(B'HCl)_2PtCl_4$.

Acetyl derivative $C_6H_4F.NHAc$. [151°]. Sl. sol. water (Wallach a. Heusler, *A.* 243, 222).

FLUORO-BENZENE C_6H_5F. Mol. w. 96. (85°). S.G. $\frac{20}{4}$ 1·0236. μ_D 1·46773 (Wallach a. Heusler, *A.* 243, 219). V.D. 3·13 (calc. 3·06).

Formation.—1. By heating potassium

fluoro-benzene sulphonate with conc. HClAq (Paternò a. Oliveri, *G.* 13, 533).—2. By decomposing diazobenzene piperidide with conc. aqueous hydrofluoric acid, the escaping gases being very well cooled (Wallach, *A.* 235, 255).

Properties.—Liquid which solidifies in ether and solid carbonic acid. The so-called fluoro-benzene described by Schmitt a. Gehren (*J. pr.* [2] 1, 394) was phenol.

p-**Di-fluoro-benzene** $C_6H_4F_2$[1:4]. (88°). S.G. 1·11. Formed by decomposing *p*-fluoro-benzene diazo-piperidide with hydrofluoric acid (Wallach a. Heusler, *A.* 243, 224). Liquid solidifies at a very low temperature.

p-**FLUORO-BENZENE SULPHONIC ACID** $C_6H_4F.SO_3H$[1:4]. From *p*-amido-benzene sulphonic acid by displacing NH_2 by F (Lenz, *B.* 10, 1137; 12, 580). The salts are v. e. sol. water and alcohol.

Chloride $C_6H_4F.SO_2Cl$. [36°]. Trimetric tables or long needles; sol. benzene, chloroform, and ether.

Amide $C_6H_4F.SO_2NH_2$. [123°]. Trimetric plates or long needles. Sl. sol. water and benzene, v. sol. acetone and alcohol.

o-**FLUORO-BENZOIC ACID** $C_6H_4F.CO_2H$[1:2]. Mol. w. 140. [118°]. Prepared by treating *o*-diazo-amido-benzoic acid with conc. HFAq

$$NH_2.C_6H_3(CO_2H).N_2.C_6H_4CO_2H + 2HF$$
$$= C_6H_4(NH_3F)CO_2H + C_6H_4F.CO_2H$$

(Paternò a. Oliveri, *G.* 12, 85). Colourless silky needles (from hot water). V. sol. alcohol and ether. More soluble in water than its isomerides. BaA'_2 2aq: laminæ, v. e. sol. water.—CaA'_2: laminæ, v. e. sol. water.

m-**Fluoro-benzoic acid** $C_6H_4F.CO_2H$[1:3]. [124°]. From *m*-diazo-amido-benzoic acid and conc. aqueous HF (P. a. O.). Laminæ, resembling benzoic acid.—NaA'aq: opaque scales.—AgA': colourless needles (from hot water); quickly altered by exposure.—BaA'_2 3aq: v. sol. hot water.—CaA'_2 3aq: pearly plates.

Methyl ether MeA'. (194°). Aromatic oil.

p-**Fluoro-benzoic acid** $C_6H_4F.CO_2H$ [1:4]. [182°]. Prepared by heating *p*-diazoamido-benzoic acid with concentrated aqueous hydrofluoric acid; on cooling, the greater part of the fluoro-benzoic acid separates out, while the hydrofluoride of *p*-amido-benzoic acid [211°] remains in solution (Schmitt a. Gehren, *J. pr.* [2] 1, 394; Paternò, *G.* 11, 90; 12, 85). Obtained also by oxidation of *p*-fluoro-toluene (Wallach, *A.* 235, 263). Laminæ or needles, smelling like benzoic acid, sl. sol. cold, v. sol. hot, water; v. sol. alcohol, ether, and benzene. Volatile with steam. Does not etch glass. Conc. HNO_3 gives a fluoro-nitro-benzoic acid. Conc. H_2SO_4 dissolves it without alteration.

Salts.—BaA'_2 4aq: colourless ill-defined laminæ, m. sol. hot water.—CaA'_2 3aq: large prisms.—AgA': yellow plates (from water).

Ethyl ether EtA': crystalline; may be distilled.

Di-fluoro-benzoic acid $C_6H_3F_2.CO_2H$. [232°]. Formed by the action of chromium perfluoride (from CaF_2, $K_2Cr_2O_7$ and H_2SO_4) upon benzoic acid (Jackson a. Hartshorn, *B.* 18, 1993; *Am.* 7, 343). Flat white needles, sol. hot benzene, sl. sol. hot water, nearly insol. cold water.

Salts.—A'_2Ca 3aq: long silky needles. S. ·5 at 15°.—A'_2Ba: scales. S. 1·2 at 15°.—KA'.

p-**FLUORO-BROMO-BENZENE** C_6H_4BrF[1:4]. [−15° to −20°]. (153°). S.G. ^{15} 1·593. From *p*-fluoro-aniline by diazotisation and treatment with cuprous bromide (Wallach a. Heusler, *A.* 243, 226). Oil.

p-**FLUORO-CHLORO-BENZENE** C_6H_4ClF. (131°). S.G. ^{15} 1·226. From *p*-fluoro-aniline by diazotisation and treatment with cuprous chloride (Wallach a. Hensler, *A.* 243, 225). Oil; volatile with steam. Solidifies at a very low temperature.

o-**FLUORO-CINNAMIC ACID** $C_9H_7FO_2$ *i.e.* $C_6H_4F.CH{:}CH.CO_2H$. From the sulphate of *o*-diazo-cinnamic acid and HF (Griess, *B.* 18, 961). Long needles. V. sl. sol. boiling water, v. sol. alcohol.

FLUORO-ψ-CUMENE $C_6H_2Me_3F$ [1:3:4:6]. [27°]. (175°). From diazo-ψ-cumene piperidide and conc. HFAq (Wallach a. Heusler, *A.* 243, 231). Volatile with steam.

FLUORO-HIPPURIC ACIDS $C_6H_4F.CO.NH.CH_2.CO_2H$. The fluoro-benzoic acids are transformed by the animal organisms into the corresponding fluoro-hippuric acids, and may be extracted from the urine by evaporating it to a syrup, treating with alcohol and filtering. The residue, on distillation of the alcohol, is decomposed with hydrochloric acid and taken up with ether, which on distillation leaves an oily mass from which the pure acid is obtained by conversion into the calcium salt and decomposing this salt with hydrochloric acid (Coppola, *G.* 13, 522).

o-**Fluoro-hippuric acid** [121°]. Crystallises in prismatic, iridescent needles, v. sol. ether and alcohol, sl. sol. chloroform, insol. carbon disulphide and benzene. It is decomposed by fuming hydrochloric acid into glycocoll and *o*-fluoro-benzoic acid.

m-**Fluoro-hippuric acid** [153°]. Prismatic needles, v. sol. hot water, alcohol and ether, insol. carbon disulphide and chloroform.—CaA'_2 2aq: rectangular laminæ.—PbA'_2 5aq: small laminæ.—AgA': flocculent pp.

p-**Fluoro-hippuric acid** [161°]. Pearly needles (from ether). Insol. benzene, CS_2, and chloroform, sol. alcohol, ether, and boiling water.—CaA'_2 2aq: four-sided tables, v. e. sol. water and alcohol.

p-**FLUORO-IODO-BENZENE** C_6H_4IF [1:4]. (183°). Formed by decomposing *p*-fluoro-diazo-benzene piperidide with conc. hydriodic acid (Wallach a. Heusler, *A.* 243, 227). Oil, volatile with steam, solidifies at low temperatures. Conc. HNO_3 liberates iodine with the formation of fluoro-nitro-benzene.

p-**FLUORO-NITRO-BENZENE** $C_6H_4F(NO_2)$. [24°]. (205°). S.G. 1·326. Formed from $C_6H_4(NO_2).N_2.NC_5H_{10}$ and conc. HF (Wallach, *A.* 235, 264). Formed also by nitration of fluorobenzene. Oil, heavier than water; smells like almonds.

FLUORO-*p*-OXY-BENZOIC ACID. *Methyl derivative* $C_6H_3F(OMe).CO_2H$. *Fluoro-anisic acid.* [204°]. From amido-anisic acid [181°] by the diazo- reaction (Paternò a. Oliveri, *G.* 12, 92). Colourless needles, sol. water and alcohol.

p-**FLUORO-PHENOL** $C_6H_4F.OH$ [1:4]. (187°). Formed by diazotising *p*-fluoro-aniline and boiling with water (Wallach a. Heusler, *A.* 243, 228). Solid at ordinary temperatures.

DI-FLUORO-DIPHENYL $C_{12}H_8F_2$ *i.e.* $F.C_6H_4.C_6H_4F$. [89°]. (255°). Formed by decomposing bi-diazo-diphenyldipiperidide with conc. HFAq (Wallach a. Heusler, *A.* 243, 234). Crystalline, v. sol. alcohol, ether.

p-**FLUORO-TOLUENE** $CH_3.C_6H_4F$. (117° i. V.). S.G. ^{25} ·992. Prepared by heating its sulphonic acid (obtained from (1, 4, 2) amido-toluene sulphonic acid) with conc. HClAq in sealed tubes (Paternò a. Oliveri, *G.* 13, 535). Obtained also from *p*-diazo-toluene piperidide and conc. HF (Wallach, *A.* 235, 261). Smells like benzonitrile. CrO_3 and aqueous H_2SO_4 at 160° give *p*-fluoro-benzoic acid [182°].

FLUORO-TOLUIC ACID $C_6H_3MeF.CO_2H$[4:3:1]. [161°]. From amido-toluic acid [165°] by the diazo-reaction (Paternò a. Oliveri, *G.* 12, 83). Needles, sol. water and alcohol.

FLUORSPAR. *Calcium fluoride* (*v.* vol. i. p. 665).

FOOT-MUCIN *v.* PROTEIDS, *Appendix C.*

FORMAMIDINE CH_4N_2 *i.e.* $NH_2.CH:NH$. *Amido-imido-methane. Formimidamide. Methenylamidine.* Formed from the compound $(HCN)_2 3HCl$ by decomposing it with alcohol at 100°; the products being formic ether and formamidine (Gautier, *A.* 145, 118; Claisen a. Matthews, *C. J.* 41, 266). Formed also by the action of alcoholic ammonia on formimido-ether $NH:CH.OEt$ (Pinner, *B.* 16, 357). **Hydrochloride** $B'HCl$. [81°]. Crystallises from alcohol in warty masses or in flat transparent plates. Very hygroscopic. Split up at 100° into HCN and NH_4Cl. Potash gives formic acid and NH_3. Heated with acetic anhydride and sodium acetate it yields di-acetyl-formimidamide and tri-acetyl-formamidil $C_2H_2Ac_3N_2$. [224°] (Pinner, *B.* 17, 171).

Platinochloride $B'_2H_2PtCl_6$: orange octahedra, v. sol. water.

Di-acetyl-derivative $NHAc.CH:NAc$. Formed as above and together with a dibasic isomeride by heating orthoformic ether with acetamide at 180° (Wichelhaus, *B.* 3, 2). Short thick prisms, sublimes without melting (Pinner, *B.* 16, 1660). Sl. sol. cold water, v. sl. sol. alcohol.

FORMAMIDOXIM CH_4N_2O *i.e.* $NH_2.CH:NOH$. *Isuretine. Methenyl-amidoxim.* [105°]. Mol. w. 60. Formed by the action of an alcoholic solution of hydroxylamine on a concentrated aqueous solution of HCN in the cold; the product is evaporated at 40° (Lossen a. Schifferdecker, *A.* 166, 295). Trimetric prisms (from alcohol). V. sol. water, sl. sol. cold alcohol. Its aqueous solution is alkaline in reaction and ppts. salts of Cu, Pb, and Hg. At 140° it splits up into CO_2, NH_3, and ammelide. Boiling water resolves it into formic acid, nitrogen, and NH_3; a small quantity (1 pt.) of water when heated with it (1 pt.) gives biuret, urea, guanidine, CO_2, nitrogen, and NH_3. Dilute acids split it up into formic acid, NH_3, and hydroxylamine.

Salts.—$B'HCl$. [60°]. Very deliquescent trimetric tables, sl. sol. alcohol.—$B'_2H_2SO_4$: needles, v. e. sol. water.—$B'H_2C_2O_4$: flat prisms, m. sol. water.—$B\,C_6H_2(NO_2)_3OH$: yellow prisms; m. sol. water and alcohol.—$CH_2N_2OHgHgCl_2$: yellow flocculent pp. got by adding $HgCl_2$ to a solution of formamidoxim. Explodes when heated. V. sol. HClAq.

FORM-ANHYDRO- COMPOUNDS *v.* METHENYL COMPOUNDS.

FORMIC ACID $H.COOH$. *Hydrogen carboxylic acid.* Mol. w. 46. [2°] (Bannoco); [8·6°] (Berthelot, Pettersson, Ekstrand). (100°) (Schiff, Landoldt, Person); (100·8°) (Zander); (101°) (Roscoe). S.G. $\frac{0}{0}$ 1·2415; $\frac{0}{4}$ 1·245; $\frac{11·4}{4}$ 1·231; $\frac{15·1}{4}$ 1·225; $\frac{19·8}{4}$ 1·22; $\frac{27·8}{4}$ 1·209; $\frac{32·8}{4}$ 1·2029 (Pettersson, *J. pr.* [2] 24, 297); $\frac{20}{4}$ 1·219 (Bruhl); $\frac{4}{4}$ 1·1829; $\frac{25}{25}$ 1·1649 (Perkin); $\frac{100·8}{}$ 1·117 (Zander). S.V. 41·08 (Schiff); 41·1 (Zander). V.D. (at 111·5°) 2·38 corresponding to molecular formula $2H_2CO_2$; (at 160°) 1·81; (at 214°) 1·62 (Pettersson and Ekstrand, *B.* 13, 1194). S.H. (0°–100°) ·519 (Pettersson). C.E. (0°–10°) ·0097; (0°–20°) ·0196; (0°–50°) ·0509; (0°–100°) ·11 (Zander, *A.* 224, 56). H.C. (at 100°) 70,750. H.F.p. 95,930. H.F.v. 95,350 (Thomson). M.M. 1·671 (Perkin). R_∞ 13·61. A^2 (*Constant of capillarity*) 5·284 (H. Schiff). *Heat of solution in water* 2·35 (sol.), ·08 (liq.) (Berthelot). *Latent heat of fusion* 57·38 (Pettersson).

Occurrence.—1. In the red ant (*Formica rufa*), from whence the acid derives its name (Marrgraf, *Diss.* Upsala, 1777).—2. In caterpillars, especially *Bombyx processionea* (Will, *J.* 1847-8, 546), and *Cerura dicranura*, the secretion of which contains 37·5 p.c. of the acid (Poulton, *B. A.* 1887, 766).—3. In various secretions of the human body, viz. the blood, spleen (Scheerer, *A.* 69, 199) and sweat (Schottin, *J.* 1852, 704).—4. In plants, viz. stinging nettles (Gorup Besanez, *A.* 72, 267), the fruit of the soap tree, *Sapindus saponaria* (*ibid. A.* 69, 369), in tamarinds, and in the needles of *Pinus abies* (Redtenbacher, *A.* 47, 148). It is also found as one of the products of oxidation of crude turpentine oil (Weppen, *A.* 34, 235; 41, 294; Laurent, *J. pr.* 27, 316).—5. In the mineral waters of Prinz Lofen (Pettenkofer, *Kastn. Archiv*, 7, 104), of Brückenau (Scheerer, *A.* 99, 257), and in the deposit from the waters of Marienbad.

Synthesis.—1. By passing carbonic oxide into damp alkali heated to 100°: $CO + KHO = KCOOK$ (Berthelot, *C. R.* 41, 955); the reaction takes place best with soda-lime heated to 190°-200°; above this temperature the formate is decomposed with production of carbonate. If the materials are dry no combination occurs (Merz and Tibiriça, *B.* 13, 23). The addition of alcohol promotes the absorption (Piritiringa, *Inaug. Diss.*, Zurich, 1879).—2. By the action of the silent electric discharge on a mixture of carbonic acid and hydrogen $CO_2 + H_2 = H_2CO_2$ (Brodie, *Pr.* 21, 245).—3. By passing a current of damp carbonic acid over metallic potassium $2CO_2 + K_2 + OH_2 = HCOOK + KHCO_3$ (Kolbe and Schmitt, *A.* 119, 251).

Formation.—1. By the oxidation of wood spirit (Dumas a. Peligot, *A.* 15, 7; Dumas a. Stas, *ibid.* 35, 137).—2. By heating wood spirit with a mixture of lime and potash (Dumas a. Stas).—3. By heating hydrocyanic acid with concentrated alkalis or mineral acids (Pelouze, *A. Ch.* [2] 48, 395; Geiger, *A.* 1, 44).—4. By the decomposition of oxalic acid by heat (Gay-Lussac, *A. Ch.* [2] 46, 218). The yield is much increased by addition of glycerin or mannite

(Berthelot, *v. infra*). An aqueous solution of oxalic acid in presence of uranic oxide is decomposed by sunlight into CO_2 and formic acid (Seekamp, *A.* 122, 113).—5. By decomposition of chloral and trihalogen derivatives of methane (Liebig, *A.* 1, 198; Dumas, *B. J.* 15, 371), or by heating chloroform with aqueous NH_3 in sealed tubes at 200°–225°, $2CHCl_3 + 7NH_3 + 3H_2O = CO + 6NH_4Cl + HCOONH_4$ (André, *C. R.* 102, 553).—6. By adding sodium amalgam to a strong aqueous solution of ammonium carbonate

$$(NH_4)_2CO_3 + Na_2 = HCO_2Na + 2NH_3 + NaOH$$

(Maly, *A.* 135, 119).—7. By distilling starch, sugar, and various albuminous substances with manganese peroxide and sulphuric acid (Döbereiner, *A.* 3, 144; Gmelin, *P.* 16, 55). Other organic substances, such as tartaric acid, gum, linseed oil, woody fibre, and cereal grains, yield formic acid when distilled with concentrated sulphuric acid with or without manganese peroxide. 8. By the electrolysis of water through which a current of CO_2 is passed (Royer, *Z.* 1870, 318). 9. By the oxidation of coal-gas by ozone (Maquenne, *Bl.* [2] 37, 298).—10. By heating alcohol with nitric acid (Gaultier de Clanbry, *J. Ph.* 25, 764).—11. By oxidation of tri-methylamine with alkaline permanganate (Wallach a. Claisen, *B.* 8, 1238).—12. By the oxidation of carbon (from carbon disulphide) with potassium permanganate (Chapman, *C. J.* 5, 133).—13. As an iron-salt by heating carbon disulphide with water and iron filings (Loew, *B.* 13, 324).—14. By heating lactic acid with sulphuric acid (Erlenmeyer).

Additional references.—Hulse and Fisher, *T.* 1670, vol. v. 2063; Wöhler, *P.* 15, 307; Hünefeld, *J. pr.* 7, 44; Guckelberger, *A.* 64, 39; Stenhouse, *P. M.* [3] 18, 122; Sacc, *A.* 51, 214; Hlasiwetz, *J. pr.* 51, 355; Liebig, *A.* 17, 69; Gehlen, *A. Ch.* [1] 83, 208; Limpricht, *A.* 97, 361; Hurst, *C. J.* 15, 278.

Preparation.—1. By heating to 60° in a capacious retort a solution of sugar (1 pt.) in water (2 pts.) with manganese peroxide (2·5–3 pts.) and 1:1 sulphuric acid (3 pts.). One-third of the acid is added at first; when the violence of the reaction has abated the remainder of the acid is added. The acid formed is condensed in a receiver, and at the end of the action the distillate is neutralised with chalk, and the filtrate evaporated to the point of crystallisation. The calcium salt is converted into the lead salt by addition of lead carbonate, and the lead salt decomposed by the requisite quantity of sulphuric acid.—2. By heating equal parts of anhydrous glycerin (or mannite) and crystallised oxalic acid in a retort to 75°–90°, until carbonic acid is no longer evolved. A fresh portion of oxalic acid is then added, and the distillation continued. This process may be repeated several times. The distillate finally contains 55 p.c. of the acid, and is redistilled over anhydrous oxalic acid when a 75 p.c. acid is obtained. This is neutralised with sodium carbonate, the dry sodium salt distilled with anhydrous oxalic acid, when a 99 p.c. acid is obtained (Lorin). The last trace of water is removed by distillation over boric anhydride, or the acid is subjected several times to a freezing mixture, the crystals separated from the liquor, and then allowed to melt, or the dry lead (or copper) salt is heated at 130° in a current of dry hydrogen sulphide; in the latter case the product is apt to be contaminated with sulphur products (Liebig; Wöhler).

In the above process the crystallised oxalic acid decomposes into water, carbonic acid and formic acid, the last of which combines with the glycerin to produce monoformin, which is subsequently decomposed by water into glycerin and formic acid, the equation being

$$C_3H_5(OH)_3 + H_2C_2O_4$$
$$= C_3H_5(OH)_2(OCHO) + H_2O + CO_2$$
$$= C_3H_5(OH)_3 + H_2CO_2 + CO_2.$$

The details of the process have been worked out by Lorin, *Bl.* [2] 5, 7, 12; 20, 241; 24, 22, 436; 25, 517; 37, 104.

Properties.—The acid solidifies below 0° and exhibits the phenomenon of superfusion. The liquid acid is colourless, transparent, and mobile. It has a pungent sour taste and odour, and when concentrated blisters the skin (Liebig).

The vapour pressure of the acid at various temperatures has been determined by Landoldt (*A. Suppl.* 6, 154) and Richardson (*C. J.* 49, 765), some of whose results are given below:—

Temperature.	Pressure in mm.	Temperature.	Pressure in mm.
5·7	13·46 R.	45	102·7 L.
10	18·4 L.	60	191·2 L.
10·2	17·44 R.	70	280 L.
20	31·4 L.	80	399·8 L.
29·7	48·33 R.	82·7	391·2 R.
30	51·6 L.	90	558 L.
40	82·3 L.	91·2	529·3 R.
44·5	82·97 R.		

Aqueous acid.—Formic acid mixes in all proportions with water. By distillation of aqueous formic acid at standard pressure a 77 p.c. acid (107°) is finally obtained, whatever the original strength: this corresponds to an acid of molecular composition $HCOOH + H_2O$, and has been termed orthoformic acid $CH(OH)_3$, the ethereal salts of which are described below. But on alteration of pressure the composition as well as the boiling-point alter; thus at 1350 mm. an 80 p.c. acid (124·1°), and at 1830 mm. an 83 p.c. acid (134·6°) finally distil (Roscoe, *C. J.* 15, 270). Perkin (*C. J.* 49, 778) also concludes that the so-called hydrate S.G. $\frac{4}{4}$ 1·1829 is only a mixture of the acid and water.

A 30 p.c. aqueous acid has the maximum electric conductivity (Hartwig, *W.* 33, 58).

Reactions.—1. The acid is completely resolved by strong *sulphuric acid* into carbonic oxide and water (Döbereiner); this reaction at a temperature of 60°–80° starts at first slowly, reaches a maximum and then decreases at a rate proportional to the mass of acid undergoing decomposition (Veley, *T.* 1888, 274, 286–297).—2. The vapour of the concentrated acid burns with a dull blue flame (Liebig).—3. It is slowly burnt when dropped on platinum black (Döbereiner).—4. Gradually oxidised by *chlorine* (Cloez), more rapidly by aqueous iodic or periodic acid (Benckieser, *A.* 17, 258; Millon, *C. R.* 19, 271). 5. Decomposed by *nitric acid* (Arvidson).—6. Heated with *zinc-dust* it is decomposed into carbonic oxide and hydrogen (Jahn, *M.* 1, 679).—7. Forms with *bromine* in presence of carbon disulphide an unstable addition product, which decomposes into HBr and CO_2 (Hell a. Mühlhaüser, *B.* 11, 245).—8. On *electrolysis* it yields O_2, H_2 and as a secondary product acetic acid (Bourgoin, *A. Ch.* [4] 14, 185).—9. Decomposed by silent electric discharge into CO_2, CO, and H_2, the proportion of the two former depending on the pressure (Maquenne, *C. R.* 96, 63).—10. The acid acts as a strong reducing agent, precipitating in alkaline solution the heavy metals, gold, platinum, and palladium from their solutions. With silver nitrate it precipitates silver formate, which is subsequently reduced to the metal; it converts mercuric into mercurous chloride, and only on protracted heating to metallic mercury. In acid solution it reduces potassium permanganate in the cold, and chromic acid when heated, and is thus distinguished and separated from acetic acid. It also reduces Fehling's solution. These reducing properties are attributed to the presence of the aldehydic group CHO in the acid.—11. The acid and its salts act as powerful antiseptics and anti-fermentatives (Jodin, *C. R.* 61, 1179; Hoffmann, *Inaug. Diss.*, Greisswald, 1884). Injected into the system they lower the temperature and blood pressure, and retard the heart's action (*Jahresber. Fort. Pharm.* 1879, 127).

Detection.—1. The solution supposed to contain the acid or its salts is heated with concentrated sulphuric acid, when carbonic oxide *only* is evolved.—2. With silver nitrate they give a white pp. turning brownish-black on boiling (*v. supra*).—3. With mercurous nitrate they give a white pp. turning grey from separation of the metal.

Estimation.—1. The acid or salt is heated for 1½ hours with sodium acetate and a normal solution of mercuric chloride, the excess of which is titrated with potassium iodide. Results 5 p.c. too low (Portes a. Ruyssen, *C. R.* 82, 1504).—2. By a standard solution of potassium permanganate acidified with dilute sulphuric acid.—3. By measurement of the volume of carbonic oxide given off by concentrated sulphuric acid.

Formates.—Formic acid is monobasic, the general formula of its normal salts being $R_n(HCOO)_n = R_nA_n$; double salts are also known of formula $R_nA_n.R'_nA_n$.

METALLIC FORMATES.—The salts are all soluble in water. Those of the fixed alkalis when heated are converted into the oxalates with evolution of hydrogen; those of the heavy metals yield the metal. The barium and calcium salts heated with the barium or calcium salts of the carboxylic acids yield the aldehydes, vol. i. p. 107. The salts when heated with water in sealed tubes at 175° are more or less completely decomposed, those of Ca, Mg, Mn, Fe, Co, Ni, Zn, Sn″, Pb, Cu, Hg″, Ag, yielding an oxide or carbonate with evolution of H_2, CO_2, and CO. In the case of the Co and Ni salts some of the metal separates, possessing highly magnetic properties; from the Cu salt Cu_2O separates in violet crystals mixed with the metal also in crystals (Riban, *C. R.* 93, 1023, 1082; *cf.* Berthelot, *ibid.* 1051).

The formates have been examined by Göbel, Schweig, Döbereiner and Liebig; Crystallographic measurements by Heusser (*P.* 83, 37); Handl, *Sitz. W.* 42, 747; Zepharovich, *ibid.* 43, ii. 545; v. Hauer, *ibid.* 548; *cf. J.* 1861, 430; Rammelsberg, *Hand. Kryst. Chem.* 274; Voss, *Inaug. Diss.*, Königsberg, 1887; Specific Gravities, by Clarke, *B.* 12, 1399; Schröder, *B.* 14, 21; Heats of Solution and Formation, Berthelot, *C. R.* 77, 24; Refraction Equivalent, Gladstone, *Pr.* 16, 441; Kanonnikow, *J. R.* 16, 124; Dispersion (crystals), v. Lang, *Sitz. W.* 31, 105; Descloizeaux, *Ann. M.* 11, 261.

Aluminium formate, obtained by ppg. barium formate with equivalent proportion of aluminium sulphate; crystallises with difficulty, decomposed by hot water with ppn. of aluminium hydrate (Liebig).

Ammonium formate NH_4A': monoclinic crystals, $a{:}b{:}c = {\cdot}884{:}1{:}1{\cdot}269$; $\beta = 1{\cdot}269$, S.G. 1·266 (Schröder). Heat of solution −2·94. Decomposes when quickly heated to 180° into formamide and water but no hydrocyanic acid (Andreasch), while at a higher temperature hydrocyanic acid only is produced (Döbereiner).

Barium formate BaA'_2: monoclinic crystals, $a{:}b{:}c = {\cdot}765{:}1{:}{\cdot}864$ (Heusser). S.G. 3·212 (Schröder), 3·471 (Clarke). Heat of solution −2·44. S. 20 to 25 in the cold; insol. alcohol and ether.—$BaA'_2 2aq$ (Krasnicki, *M.* 8, 599).

Formonitrate $BaNO_3A' 2aq$ (Ingenhoes, *B.* 12, 1680).

Double salts. Barium-zinc $BaA'_2.ZnA'_2 2aq$: triclinic crystals, $a{:}b{:}c = {\cdot}579{:}1{:}{\cdot}452$; $\beta = 108° 49'$ (Heusser; Voss).—*Barium manganese salt* $BaA'_2.MnA'_2 2aq$: monoclinic crystals, $a{:}b{:}c = 1{:}{\cdot}759{:}917$ (Heusser).—*Barium cobalt salt* $BaA'_2CoA'_2 2aq$: triclinic, isomorphous with the barium-zinc salt, as also *Barium-nickel salt* $BaA'_2NiA'_2 2aq$, and *Barium copper salt* $BaA'_2CuA'_2 2aq$ (Heusser; Voss).—*Barium copper* $2BaA'_2.CuA'_2 2aq$: triclinic crystals, S.G. ^{20} 2·747. *Barium cadmium* $BaA'_2CdA'_2 2aq$: monoclinic crystals, $a{:}b{:}c = {\cdot}898{:}1{:}54$. S.G. $\frac{19}{4}$ 2·724.

Bismuth formate. White crystals, readily sol. water.

Cadmium formate $CdA'_2 aq$: monoclinic prisms, $a{:}b{:}c = 1{\cdot}325{:}1{:}1{\cdot}224$; $\beta = 97° 5'$ (Kopp). S.G. $\frac{20}{4}$ 2·429 (Clarke), 2·477 (Schröder), readily sol. water, dehydrated with difficulty.

Calcium formate CaA'_2: rhombic crystals, $a{:}b{:}c = {\cdot}759{:}1{:}{\cdot}467$. S.G. 2·021 (Schröder). Heat of solution ·66. S. 10 to 12·5 in the cold, insol. alcohol. Forms methyl alcohol on dry distillation.

Cerium formate $CeA' aq$, prepared by ppg. a solution of cerous chloride with sodium formate, rose-coloured, crystalline powder, converted into ceroso-ceric oxide, when heated.

Cobalt formate $CoA'_2 2aq$: rose-red crystals. S.G. ^{20} 2·1286. S. 20 at 20° Voss.

Copper formate CuA'_2: blue transparent monoclinic crystals, $a{:}b{:}c = 1{:}{\cdot}996{:}{\cdot}771$. S.G. 1·831 (Schröder). Heat of solution −7·84 (hydrated), ·52 (anhydrous). Prepared by neutralising formic acid with copper carbonate or freshly ppd. oxide, and spontaneously evaporating. If the solution is heated the basic salt separates out. S. 12·5 to 25 in the cold. S. (80 p.c. alcohol) ·25.

Basic salt $CuA'_2 2Cu(OH)_2$: pale-green powder, insoluble; prepared by boiling an aqueous solution of the normal salt.

Double salts. Copper hydrogen $CuA'_2HA' 1\frac{1}{2}aq$: blue, rhombic, six-sided tables, $a{:}b{:}c = 1{\cdot}324{:}1{:}1{\cdot}765$, separated, together with the CuSr salt, from a strongly acid solution of 2 mols. SrA'_2 and 1 mol. CuA'_2 (Zepharovich). *Copper strontium* $2SrA'_2.CuA'_2.8aq$: triclinic crystals, $a{:}b{:}c = {\cdot}744{:}1{:}1{\cdot}0103$ (Zepharovich), and

$SrA'_2CuA'_2$4aq. S.G. ^{22} 2·133 (hydr.), 2·612 (anhyd.), Schröder.

Didymium formate DiA'_3. S.G. 3·43. S.V.S. 80·8. Violet powder, v. sl. sol. water (Clève, *Bl.* [2] 43, 365).

Erbium formate $Er_2A'_6$4aq: red crystals (Clève, *C. R.* 91, 382).

Iron formates. *Ferrous formate* FeA'_2.2aq, v. sl. sol. water (Scheurer-Kestner, *A. Ch.* [3] 68, 480).

Ferric formate FeA'_3aq: yellow glistening crystals, obtained by dissolving recently precipitated ferric hydrate in formic acid; from its solution ferric hydrate gradually separates, while a basic salt remains in solution (Scheurer-Kestner; *cf.* Ludwig, *J.* 1861, 433). *Formo-nitrate* $Fe_2A'_3(NO_3)(OH)_2$ 3aq: yellow crystals, readily decomposed. *Formo-chloride* $Fe_2A'_4Cl_2$ 3aq: reddish-yellow salt, v. sl. sol. water (Scheurer-Kestner).

Lead formate PbA'_2: rhombic prisms or needles, isomorphous with barium salt (Heusser). S.G. 4·571 (Bödeker, *J.* 1860, 17; Schröder). Heat of solution $-3·45$. S. 1·6 at 16°, 18 at 100° (Barfoed, *Z.* 1870, 272). Insol. alcohol, thus differing from lead acetate. The dry salt decomposes at 190°, thus $Pb(CHO)_2 = 2CO_2 + H_2 + Pb$. *Basic salts.* By boiling aqueous solution with lead oxide the following basic salts separate out. PbA_2PbO, prisms, sol. 58·5 pts. cold water, PbA_22PbO. Sol. 25·5 pts. cold, 7·5 pts. water (100°), of strong alkaline reaction, PbA_33PbO crystalline pp. sol. 90 pts. cold water (Barfoed).

Formonitrate $3PbA'_2Pb(NO_3)_2$ 2aq: rhombic tables, v. sl. sol. (Lucius, *A.* 103, 115).

Lithium formate LiA'_2aq: rhombic crystals, *a*:*b*:*c* = 1:·651: 484 (Handl). S.G. 1·435–1·479 (Schröder).

Magnesium formate $MgA'_2$2aq: rhombic prisms and octahedra. S. 7·7, insol. alcohol and ether (Souchay a. Groll, *J. pr.* 76, 470).

Manganese formate $MnA'_2$2aq: monoclinic crystals, *a*:*b*:*c* = 1·317:1:1·213; $\beta = 97° 38'$ (Heusser; Voss). S.G. 1·953 (hydr.), 2·205 (anhyd.) (Schröder).

Mercurous formate $Hg_2A'_2$: glistening scales. S. ·4 at 17°, decomposed when boiled with water, $Hg_2(CHO_2)_2 = Hg_2 + H_2CO_2 + CO_2$ (Göbel).

Nickel formate $NiA'_2$2aq: green crystals. S.G. ^{20} 2·1547 (Clarke).

Potassium formate KA'. Deliquescent, rhombic cubes. S.G. 1·908. [150°]. Heat of solution $-·93$.

Samarium formate SmA'_3: white powder, v. sl. sol.

Silver formate AgA': crystalline pp. formed by adding silver nitrate to an alkaline formate, completely decomposed on boiling with water, $2AgCHO = Ag_2 + CO_2 + H_2CO_2$, thus differing from the acetate.

Sodium formate NaA'_2: rhombic prisms, *a*:*b*:*c* = ·919:1:·97; $\beta = 58° 9'$ (Fock, *Z. K.* 7, 61). M.P. 200°. M. sol. (water), sl. sol. (alcohol), insol. (ether). S.G. 1·919 (Schröder). Heat of solution $-·52$. Decomposed when heated into hydrogen and the oxalate: $2NaCHO_2 = H_2 + Na_2C_2O_4$. – NaA_2.aq, rhombic tables, sol. 2 pts. (water). The acid salts of sodium and potassium described by Bineau do not exist.

Strontium formate $SrA'_2$2aq: rhombic crystals, *a*:*b*:*c* = ·608:1:·595 (Heusser), exhibiting hemihedral forms (Pasteur, *A. Ch.* [3] 31, 98; Jacobsen, *P.* 113, 493). S.G. 2·25 (hyd.), 2·667 (anhyd.) (Schröder). Heat of solution 2·73 (hyd.), ·31 (anhyd.), m. sol. (water).

Terbium formate, white powder. M. sol. water.

Thallium formate TlA'_2: v. sol. water; melts below 100° without decomposition (Kuhlmann, *C. R.* 55, 607).

Thorium formate ThA'_1.4aq: tables, deliquescent (Chydenius, *P.* 119, 54).

Ytterbium formate $YC_2A'_3$4aq: crystalline aggregates (Marignac, *A. Ch.* [5] 14, 247.

Yttrium formate, very soluble, deliquescent. The philippium formate described by De lafontaine, *A. Ch.* [5] 14, 238 is probably a mixture of terbium and yttrium formates, which separates in rhombic prisms, *a*:*b*:*c* = ·89:1:1·484 (Roscoe, *C. J.* 41, 281).

Zinc formate $ZnA_2$2aq: monoclinic crystals, isomorphous with Mn salt. S.G. 2·151 (hyd.) (Schröder); $\frac{21·8}{4}$ 2·157 (Clarke), 2·306 (anhyd.). Heat of solution $-1·2$ (hyd.), 1·97 (anhyd.).

ALKYL FORMATES. *Formic ethers.*

Methyl ether $C_2H_4O_2$ or MeA'. Mol. w. 60. S.G. $\frac{32·3}{4}$ ·957 (S.); $\frac{0}{4}$ ·978 (E.); $\frac{15}{15}$ ·982, $\frac{25}{25}$ ·969 (Perkin); ^{15} ·979 (Grodzki a. Krämer). V.D. 2·084 (for 2·08) (Dumas a. Peligot). C.E. (0°–10°) ·00144 (E.). S.V. 62·57 (S.), 62·84 (E.), 63·2 (Ramsay). H.C.v. 241,620 (Thomson), 238,700 (Berthelot). H.F.p. 89,430. H.F.v. 88,270. M.M. 2·495 at 16° (P.). A^2 4·944 (S.).

Occurrence.—In crude wood spirit (Mabery, *A. C. J.* 5, 259).

Preparation.—1. By adding calcium formate (100 pts.) gradually to wood spirit (130 pts.), saturated with hydrochloric acid. The distillate is poured back, redistilled, and finally rectified over sodium carbonate and calcium chloride (Volhard, *A.* 176, 133).—2. By distilling a mixture in equivalent proportions of sodium formate, hydrochloric acid, and wood spirit (Bardy a. Bordet, *A. Ch.* [5] 16, 561; *cf.* Dumas a. Peligot, *A. Ch.* [2] 58, 48).

Properties.—Colourless liquid of ethereal odour.

Mono-chloro-methyl formate HCO_2CH_2Cl. Prepared by passing chlorine in the dark at 100° into methyl formate.

Perchloromethyl formate $ClCO_2CCl_3$ (180°–185°). S.G. ^{10} 1·724 (Cahours, *A.* 64, 315). When passed through a strongly heated tube it is converted into carbon oxy-chloride. With alcohol it forms ethyl chloro-formate, the equation being $C_2Cl_4O_2 + 2EtOH = 2ClCO_2Et + 2HCl$.

Ethyl ether $C_3H_6O_2$ or EtA'. Mol. w. 74. (53·5°) at 754·5 mm. (R. Schiff); (55°) (Gartenmeister); (54·4°) (Elsässer). S.G. $\frac{0}{0}$ ·945 (G.); $\frac{0}{4}$ ·937 (Elsässer); $\frac{20}{4}$ ·9064 (Brühl); $\frac{15}{15}$ ·9298, $\frac{25}{25}$ ·9188 (Perkin); $\frac{53·4}{4}$ ·873 (S.) (*cf.* Naccari a. Pagliani, *W. Beibl.* 687). V.D. 2·593 (for 2·565) (Liebig). C.E. (0°–10°) ·001331 (E.). S.V. 84·57 (S.); 84·6 (G.); 85·14 (E.). μ_β 1·3642. R_∞ 28·61 (B.). M.M. 3·564 at 18·8. H.F.p. 95,900. H.F.v. 94,160. A^2 4·528. *Critical Temperature* 238·6° (Pawlewski).

Preparation.—1. By distilling a mixture of

90 p.c. alcohol (6 pts.), sodium formate (7 pts.), and concentrated sulphuric acid (10 pts.) (Liebig, *A.* 17, 72).—2. By heating a mixture of glycerin, oxalic acid, and alcohol in a reflux apparatus, and then distilling (Lorin, *Bl.* [2] 5, 12).—3. Starch (9 pts.) mixed with manganese peroxide (29 pts.), is added to a mixture of sulphuric acid (20 pts.), water (5 pts.), and 85 p.c. alcohol (15 pts.), and the whole distilled (Stinde, *D. P. J.* 181, 402).—4. As a secondary product in the preparation of ethyl oxalate (*J. pr.* 83, 1), its formation being due to the decomposition of mono-ethyl oxalate (Anschütz, *B.* 16, 2412).

Properties. — Liquid, of odour resembling peach-kernels. S. 11 at 18°, sol. alcohol and ether. Vapour-tension at various temperatures (Naccari a. Pagliani):—

Temp.	Pres.	Temp.	Pres.
20·2	193·7	50·3	656·9
31·2	311·2	55·1	782·2
40·87	459·9	60·5	941·9

Reactions. — Decomposed by sodium or sodium-ethylate into carbonic oxide and alcohol $HCO_2Et = CO + EtOH$ (Geuther, *Z.* 1868, 665). With chlorine it yields *di-chloro-ethyl formate* $HCO_2C_2H_3Cl_2$, S.G. $\frac{16}{}$ 1·261, which is decomposed when boiled, and by alkalis into KCl, potassium formate, and acetate (Malaguti, *A.* 32, 39); and *per-chloro ethyl formate* $ClCO_2C_2Cl_5$ (*cf.* TRICHLORACETIC ACID) (Bucholz, *Crell. N. Entdeck.* 6, 55; Gehlen, *S.* 4, 18; Dobereiner, *A.* 3, 145; Kopp, *A.* 55, 180).

Propyl ether PrA′. Mol. w. 88. (81°) at 760 mm. (Gartenmeister, Elsässer, Schumann); (82·5°–83°) at 763·4 mm. (Schiff). S.G. $\frac{0}{0}$ ·925 (G.); $\frac{0}{4}$ ·9184 (E.); $\frac{0}{}$ ·9188 (Pierre a. Puchot); $\frac{15}{15}$ ·9099, $\frac{25}{25}$ ·9002 (Perkin); $\frac{82\cdot5}{4}$ ·8075 (S.). C.E. (0°–10°) ·001212 (E.); (0°–20°) ·0246 (Pierre a. Puchot). S.V. 108·7 (S.); 106·2 (G.); 106·8 (E.). H.F.p. 102480. H.F.v. 100160. M.M. 4·534. A^2 4·486. S. 2·2 at 22° (Traube, *B.* 17, 2304). *Critical temperature*, 267·4 (Pawlewski; Pierre a. Puchot, *A.* 153, 262; 163, 271).

Isopropyl ether PrA′. (68°–71°). S.G. $\frac{0}{}$ ·8826 (Pribram a. Handl, *M.* 2, 685). Specific viscosity 31·5 at 10·4°.

n-Butyl ether $HCO_2C_4H_9$. (104°–105°) at 739·4 mm. S.G. $\frac{0}{}$ ·9058. Specific viscosity 52 at 1·9° (Pribram a. Handl, *ibid.* 692).

Isobutyl ether. (97·9°) at 760 mm. (Schumann, Elsässer); (98·5°) at 759·8 mm. (Schiff). S.G. $\frac{0}{4}$ ·8854 (E.); $\frac{0}{}$ ·8845 (Pierre a. Puchot); $\frac{98\cdot4}{4}$ ·7784 (S.). S.V. 127·6 (G.); 130·7 (S.); 129·9 (E.). S. 1 at 22° (Traube, *B.* 17, 2304). C.E. (0°–10°) ·00112 (E.; *cf.* Pierre a. Puchot, *A.* 163, 281). H.F.p. 106,700. H.F.v. 103,800. A^2 4·064 (S.) (Wurtz, *A.* 93, 121).

Iso-amyl ether $HCO_2C_5H_{11}$. Mol. w. 116. (123·3°) at 760 mm. (Schumann, Schiff, Elsässer); (130·4°) (Gartenmeister). S.G. $\frac{0}{0}$ ·9018 (G.); $\frac{0}{4}$ ·8944 (E.); $\frac{20}{4}$ ·8802 (Brühl); $\frac{123\cdot6}{4}$ ·7554 (S.). S.V. 153·2 (S.); 150·21 (E.); 150·5 (G.). C.E. (0°–10°) ·00107 (G.). μ_β 1·4027. R_∞ 51·06 (B.). *Critical temperature* 304·6. A^2 4·149 (S.). Prepared by distillation of glycerin, oxalic acid, and fusel oil.

Hexyl ether $HCO_2C_6H_{13}$. (153·6°) (Gartenmeister); (146°) (Frentzel). S.G. $\frac{0}{0}$ 8977 (G.); $\frac{17}{}$ ·8495 (F.). S.V. 173·3 (G.). C.E. (0°–10°) ·00106 (G.).

Heptyl ether $HCO_2C_7H_{15}$. (176·7°) (Gartenmeister). S.G. $\frac{0}{0}$ ·8937 (G.). S.V. 196·7 (G.). C. E. (0°–10°) ·00097.

Octyl ether $HCO_2C_8H_{17}$ (198·1°) (G.). S.G. $\frac{0}{0}$ ·8929 (G.). S.V. 220·3 (G.). C.E. (0°–10°) ·00096.

Allyl ether $HCO_2C_3H_5$. Mol. w. 86. (82·83°). S.G. $^{7\cdot5}$ ·9322 (Tollens, *Z.* 1866, 518; 1868, 441). H.F.p. 65,020. H.F.v. 63,280. Formed as a subsidiary product in the preparation of formic acid from glycerin and oxalic acid when the mixture is not too strongly heated.

Phenyl ether HCO_2Ph. (180° with decomposition). Phenol and formic acid (equiv. pts.) are heated at 80° and $POCl_3$ ($\frac{1}{3}$ equiv.) slowly added (Seifert, *J. pr.* [2] 31, 467).

ORTHOFORMIC ACID. As stated above, though orthoformic acid $HC(OH)_3$ has not been isolated as such, its ethereal salts are stable compounds, prepared by heating chloroform with the alcohol in presence of an alkali metal or hydrate $CHCl_3 + 3RONa = 3NaCl + CH(OR)_3$ (Williamson a. Kay, *Pr.* 7, 135).

Methyl ether $HC(OMe)_3$. (101°–102°) (Deutsch, *B.* 12, 117); (102°) (Pinner, *B.* 16, 1644). S.G. $\frac{23}{}$ ·974 (D.). V.D. 52·59 (obs.). H.F.p. 130,460. H.F.v. 127,270. Prepared from methyl alcohol, chloroform, and sodium.

Ethyl ether $HC(OEt)_3$. (145°–146°) (Kay); (146°–148°) (Ladenburg a. Wichelhaus, *A.* 152, 164); (147°–149°) (Deutsch); (145°) (Pinner). S.G. ·894.

Formation.—1. From chloroform and sodium ethylate (Williamson a. Kay).—2. By decomposing the hydrochloride of formimido-ether with alcohol (Pinner).

Preparation.—1. Sodium ethylate free from alcohol is mixed with a little ether and chloroform added slowly. The mixture is warmed on a water-bath, then distilled and rectified over $CaCl_2$ (Stapff, *Z.* 1871, 186).—2. Sodium (7 pts.) is added gradually to a mixture of $CHCl_3$ (12 pts.), absolute alcohol (14 pts.), and a little ether (Wichelhaus a. Ladenburg, *A.* 152, 164; Deutsch, *B.* 12, 116; *cf.* Bassett, *C. J.* 2, 198).

Properties.—Liquid of aromatic odour; liquid at −18°; v. sol. water.

Reactions.—1. Heated with acetic acid it is decomposed into formic acid and ethyl acetate (Sawitsch, *J.* 1860, 391).—2. By sodium ethylate it is converted into CO, alcohol, ether, and formic acid (Bassett).—3. With bromine it gives EtBr, alcohol, ethyl formate, and ethyl carbonate, according to the equation: $2HC(OEt)_3 + Br_2 = 2EtBr + HCO_2Et + CO(OEt)_2 + EtOH$.

Dimethyl ethyl ether $CH(OMe)_2OEt$. (115°–120°). Prepared by mixing the hydrochloride of formimido-ether with methyl alcohol (Pinner, *B.* 16, 356).

Tripropyl ether $CH(OPr)_3$. (196°–198°) (Deutsch); (194°) (Pinner). S.G. $\frac{23}{23}$ ·879. V.D. 95·64 (D.).

Dipropyl methyl ether $HC(OPr)_2OMe$. (181°) (P.).

Dipropyl ethyl ether $HC(OPr)_2OEt$. (186°) (P.).

Dimethyl propyl ether $HC(OMe)_2OPr$. (152°) (P.).

Diethyl propyl ether $HC(OEt)_2OPr$. (167°) (P.).

Dipropyl isoamyl ether $HC(OPr)_2OC_5H_{11}$. (226°) (P.).

Propyl di-isobutyl ether $HC(OPr)(OC_4H_9)_2$. (208°) (P.).

Tri-isobutyl ether $HC(OC_4H_9)_3$. (220°–222°). S.G. $\frac{23}{23}$ ·861. V.D. 114·86 (Deutsch).

Dibutyl isoamyl ether $HC(OC_4H_9)_2(OC_5H_{11})$. (232°) (P.).

Di-isoamyl ethyl ether $HC(OC_5H_{11})_2OC_4H_9$. (254°) (P.).

Triallyl ether $CH(OC_3H_5)_3$. (196°–205°). Prepared from sodium (16 g.), allyl alcohol (35 g.), and chloroform (24 g.), diluted with double its volume of petroleum (Beilstein a. Wiegand).

Phenyl ether $CH(OPh)_3$. [72°] (Tiemann, *B.* 15, 2686); [76°–77°] (Auwers, *B.* 18, 2657). (270° at 55 mm.) (T.). Long needles; insol. water, sol. ether, chloroform, and benzene. Formed by the action of chloroform on alkaline phenol solution. Readily decomposed by acids, not by alkalis.

o-Nitro phenyl ether $CH(OC_6H_4NO_2)_3$. [182°]. From chloroform (2 mols.) and potassium *o*-nitro phenol (3 mols.), heated to 150°. Yield small. Needles (Weddige, *J. pr.* [2] 26, 445).

p-Nitro phenyl ether. [232°]. Needles. Prepared as above (Weddige).

Formamide CH_3NO *i.e.* $HCONH_2$. *Amide of formic acid.* Mol. w. 48. (192°–195°) with decomposition into carbonic oxide and ammonia; (140° *in vacuo*) (Hofmann, *C. J.* 16, 72); (208°) (Claisen a. Matthews, *C. J.* 41, 264); (150° *in vacuo*) (Schulze, *J. pr.* [2] 27, 516).

Formation.—1. By heating ethyl formate with ammonia (Hofmann).—2. By heating ammonium formate together with urea at 140° (Berend, *A.* 128, 335): $2HCO_2NH_4 + CO(NH_2)_2 = 2HCO_2NH_2 + (NH_4)_2CO_3$.—3. By the action of sodium-amalgam on a solution of potassium cyanate (Basarow, *B.* 4, 409).—4. By the action of strong fuming HCl on HCN (Claisen a. Matthews).

Preparation.—1. Ammonium formate is heated at 230° for five hours under pressure, yield 71 p.c. of theoretical (Hofmann, *B.* 15, 980).—2. By heating dry formic acid (55 g.) with ammonium sulphocyanide (31 g.) for two days, and then distilling *in vacuo*. Yield 74 p.c.

Properties.—Liquid, sol. water, alcohol and ether.

Reactions.—1. Decomposed by alkalis in the cold with evolution of NH_3.—2. Split up by PCl_5 into CO and a little HCN (Wallach, *B.* 15, 210).—3. With P_2O_5 it yields HCN (Hofmann). 4. It absorbs dry HCl in the cold with formation of a crystalline addition product, which at a higher temperature is completely resolved into NH_4Cl and CO.—5. With bromine in equimolecular proportions in presence of soda it forms a crystalline bromo-derivative HCONHBr, decomposed into HBr and $H_3C_3N_3O_3$ (Hofmann, *B.* 15, 753).—6. With ethyl aceto-acetate in presence of zinc chloride it yields di-methyl-ethyl-pyridine carboxylic ether (Canzoneri a. Spica, *G.* 14, 448).

Methyl-formamide HCONHMe. (190°) S.G. $\frac{19}{19}$ 1·011. Formed by evaporating an aqueous solution of methylamine formate, and distilling the residue. Liquid, sol. water and alcohol, insol. ether. Decomposed by alkalis and acids into formic acid and $NMeH_2$; by P_2O_5 into CO, HCN, and NH_2Me; and by $ZnCl_2$ into NH_3, CO and hydrocarbons (Linnemann, *Sitz. W.* [2] 60, 46).

Ethyl-formamide HCONHEt. (196°–197°). S.G. ^{21} ·952. Formed in the same way as the above. Liquid, sol. water and alcohol, insol. ether. Resembles the above in its reactions (Linnemann, *ibid.* 48).

Diethyl-formamide $HCONEt_2$ (175°–178°) (Linnemann, *Sitz. W.* [2] 60, 51); (178°) (Wallach a. Kamensky, *A.* 214, 240). S.G. $\frac{19}{}$ ·908 (L.). Prepared by distilling diethyl-amine formate (L.) (W. a. K.), or diethyl-oxamic acid (W. a. K.). Liquid, sol. water, but separated by KHO and K_2CO_3.

Salt.—$(B'HCl)_2PlCl_4$: yellow pp.

Reactions.—1. With acids, alkalis and $ZnCl_2$ it behaves like the above compounds (Linnemann).—2. PCl_5 gives $HCCl_2NEt_2$ which splits up thus $2HCCl_2NEt_2 = 3HCl + C_{10}H_{19}ClN_2$. The product is a base forming a salt $(B'HCl)_2PtCl_4$ and decomposed when heated with formation of pyrrole (Wallach a. Kamensky).

Isopropyl-formamide HCONHPr. (220°). From isopropyl-carbamine and HCl in the cold (Gautier, *A.* 149, 158).

Phenyl-formamide $HCONHC_6H_5$. *Formanilide* [46°].

Formation.—By distillation of equimolecular proportions of aniline and oxalic acid (Gerhardt, *A.* 60, 310; Hofmann, *A.* 142, 121), $C_2H_2O_4 + NH_2Ph = HCONHPh + CO_2 + H_2O$.

Preparation.—By heating aniline and formic acid (equimols.). The product is heated on a water-bath under reduced pressure to remove the water, then distilled at ordinary pressure up to 250°. The contents of the retort are then poured out (Tobias, *B.* 15, 2443, 2866; Wallach a. Wüsten, *B.* 16, 145).

Properties.—Long needles or four-sided prisms, m. sol. water, sol. alcohol; exhibits phenomenon of superfusion.

Reactions.—1. Decomposed by dilute acids into aniline and formic acid.—2. Split up by concentrated HCl into benzonitrile $HCONHPh = PhCN + H_2O$.—3. If gaseous HCl is passed in at 100° the amide is decomposed into formic acid and diphenyl-formamidine CHNPhNHPh. 4. By conc. H_2SO_4 it is decomposed into CO and amido-benzene *p*-sulphonic acid.—5. With zinc-dust it yields CO, CO_2, H_2, aniline and benzonitrile (Gasiorowski a. Merz, *B.* 18, 1002).—6. Heated with phenyl cyanate at 180° it yields phenyl-carbamine, di-phenyl-urea and CO_2 (Kühn, *B.* 18, 1477).—7. Converted by alcoholic solutions of alkyl bromides (1 mol.) followed by alcoholic KOH (1 mol.) into alkyl-formanilides (Pictet a. Crépieux, *B.* 21, 1106).

Sodium formanilide HCONNaPh aq. Formed by adding conc. soda to formanilide (Hofmann). Glistening plates; v. sl. sol. alcohol; decomposed by water (Tobias, *B.* 15, 2443).

Nitroso-formanilide HCON(NO)Ph. [39°]. Formed by passing nitrous acid into a cooled solution of formanilide in acetic acid. Yellowish-white needles, v. sol. water; readily decomposed.

Methyl-formanilide HCONMePh (P.); (253°) at 716 mm. (P. a. C.). S.G. $\frac{18}{4}$ 1·097. Formed from the hydrochloride of formimido-ether and methyl aniline, the reaction being as follows: NH:CHOEt.HCl + NHMePh + H_2O = HCONMePh + EtOH + NH_4Cl (Pinner, *B.* 16, 1652; P. a. C.).

Ethyl-formanilide H.CO.NPhEt. (258° i.V.) at 728 mm. S.G. $\frac{16}{4}$ 1·063.

Propyl-formanilide H.CO.NPhPr. (267° i.V.) at 737 mm. S.G. $\frac{16}{4}$ 1·044.

Isopropyl-formanilide H.CO.NPhPr. (263° i.V.) at 720 mm.

Isobutyl-formanilide $H.CO.NPh.C_4H_9$. (274° i.V.) at 731 mm.

Isoamyl-formanilide $H.CO.NPhC_5H_{11}$. (286° i.V.) at 728 mm. S.G. $\frac{16}{4}$ 1·004.

Phenyl-formanilide $HCONPh_2$. *Diphenyl-formamide.* [73°–74°]. (210°–220° *in vacuo*). Formed from diphenylamine and formic or oxalic acid. When heated with $ZnCl_2$ yields acridine (Willm a. Girard, *B.* 8, 1196).

Formo-o-toluide $HCONHC_6H_4Me$. [58°] (Tobias, *B.* 15, 2446); [56·5°–57·5°] (Ladenburg, *B.* 10, 1129). (288°) (L.). Formed from *o*-toluidine and formic acid. Glistening leaflets, v. sol. alcohol. Decomposed into its constituents by dilute sulphuric acid. Heated for some time at its boiling-point it yields *o*-toluidine, methyl-ditolylamine, CO, and CO_2. **Sodium derivative** $HCONNaC_6H_4Me$ aq.

Formo-p-toluide. [45°] (Hübner, *A.* 209, 372); [52°] (Tobias, *B.* 15, 2446). Formed (1) as the above (T.); (2) by heating *p*-toluidine oxalate (H.). Long needles, v. sol. water, and alcohol. Converted into the nitrile of *p*-toluic acid when heated with zinc-dust (*B.* 18, 1002).

Formo-m-xylide. [113°–114°]. Glistening needles or leaflets, v. sol. alcohol and ether (Gasiorowski a. Merz, *B.* 18, 1011).

Formo-cumidide $HCONHC_6H_2Me_3$. [121°]. Needles v. sl. sol. water, sol. alcohol and ether (Senier, *C. J.* 47, 768).

Formo-isobutyl-o-toluide $HCONHC_6H_3MeCH_2Pr$ [1:2:4]. [105°]. Colourless tables, v. sl. sol. water, sol. alcohol and ether (Effront, *B.* 17, 2347).

Formonaphthalides *v.* NAPHTHYL-AMINES.

Formopiperidide *v.* PIPERIDINE.

V. H. V.

FORMIC ALDEHYDE CH_2O. *Oxymethylene.* Mol. w. 30 (observed by Raoult's method: 34, Tollens a. Mayer, *B.* 21, 1566).

Formation.—1. By passing a current of air, charged with vapour of methyl alcohol, over a glowing spiral of platinum wire or over platinised asbestos; if the escaping gases are passed through a Liebig's condenser a solution of formic aldehyde in methyl alcohol will collect in the receiver (Hofmann, *Pr.* 16, 156; *cf.* Volhard, *A.* 176, 128; Kablonkoff, *Bl.* [2] 38, 379). When platinum foil at 55° is used the yield is 12 p.c. (Tollens, *L. V.* 29, 355; *C. J.* 46, 293). Red-hot oxide of iron or copper may be used instead of platinum (Loew, *J. pr.* [2] 33, 322; Tollens, *B.* 19, 2133).—2. By decomposing chloro-methyl acetate (2 pts.) with water (1 pt.) by heating for 30 minutes to 100° (Michael, *Am.* 1, 418).—3. Formed in small quantities by the action of ozone on coal-gas (Macquenne, *Bl.* [2] 37, 298).—4. In small quantity, together with formic acid and CH_4, by the action of the silent electric discharge on a mixture of hydrogen and CO_2 (Brodie, *Pr.* 22, 172).—5. When a mixture of methylal $CH_2(OMe)_2$ and H_2SO_4 is warmed, formic aldehyde is given off, but it quickly polymerises giving a sublimate of its solid modification.—6. By heating ethylene with oxygen at 400° (Schützenberger, *Bl.* [2] 31, 482).—7. In the incomplete combustion of nitric ether (Pratesi, *G.* 14, 221).

Properties.—Formic aldehyde is only known in solution; by freezing the solution and removing the ice an aqueous solution may be concentrated until it contains 10 p.c. of the aldehyde (Hofmann, *B.* 11, 1685; *cf.* Tollens, *B.* 15, 1629; 16, 917). The aqueous solution is pungent; it reduces ammoniacal $AgNO_3$, forming, when gently warmed, a silver mirror. When warmed with aqueous KOH it gives a brownish oil and an odour like that accompanying aldehyde-resin. Dilute aqueous NaOH gives formic acid and MeOH. After treating the solution with H_2S and heating the resulting liquid with conc. HClAq, it solidifies on cooling to a dazzling white mass of felted needles consisting of $(CH_2S)_3$. When evaporated with ammonia or ammonium carbonate it leaves a residue of hexamethyleneamine, by weighing which the amount of formic aldehyde in the solution may be determined (Loew, *J. pr.* [2] 33, 322; *cf.* Legler, *B.* 16, 1333). A solution of formic aldehyde deposits after some time insoluble formic paraldehyde or tri-oxy-methylene.

Reactions.—1. Readily condensed by strong *bases*, to a less extent by salts with alkaline reaction. Calcined MgO has no action. BaH_2O_2Aq gives formic acid and methyl alcohol; the BaH_2O_2 is, however, soon neutralised and ceases to act. CaH_2O_2Aq, MgH_2O_2Aq, Fe, Pb, PbO, many Pb salts, NEt_4OH, and many organic bases give rise to formose or methylenitan $C_6H_{10}O_5$. By boiling a 7 p.c. solution with tin a body resembling formose, called (β)-formose, is formed. MgH_2O_2Aq at about 100° gives at least two sugars, one of which yields an osazone in yellow needles [152°]. None of these sugars ferment with yeast. NaCl has no action alone, but increases the activity of CaH_2O_2Aq, whilst NaAcO, KNO_3, and much Cu, Fe, or Sn diminish it (O. Loew, *B.* 21, 270; *J. pr.* [2] 33, 321; 34, 51; Wehmer a. Tollens, *A.* 243, 340).—2. Readily condenses with primary amines: $CH_2O + H_2NR = H_2O + CH_2NR$. Thus methylamine, aniline, *o*-toluidine, and *p*-toluidine give methylene-methyl-amine (c. 207°), phenyl-methylene-amine $C_6H_5N:CH_2$ [138°], *o*-tolyl-methylene-amine $C_6H_4MeN:CH_2$, and *p*-tolyl-methylene-amine [c. 122°] respectively (Kolotoff, *Bl.* [2] 45, 253; Tollens, *B.* 17, 657; Wellington a. Tollens, *B.* 18, 3309). These formulæ ought, perhaps, to be doubled. Primary and secondary bases also give compounds of the form $CH_2(NHR)_2$ and $CH_2(NRR')_2$, thus: aniline and di-ethyl-amine give di-phenyl-methylene-diamine $CH_2(NHPh)_2$ [49°], and methylene-tetra-ethyl-diamine $CH_2(NEt_2)_2$ (167°) respectively (Pratesi, *G.* 14, 353; Kolotoff, *Bl.* [2] 43, 112; Ehrenberg, *J. pr.* [2] 36, 118). In these condensations with bases the paraldehyde may be used.—3. By boiling with a solution of *ammonium chloride* it is converted into NMe_3 and CO_2 (Plöchl, *B.* 21, 2117). 4. By heating a 16 p.c. solution of formic aldehyde with *ammonium sulphate* on the water-bath CO_2 is given off and the sulphates of mono-, di-, and tri-methylamine are formed. If *methyl-*

amine or *dimethylamine hydrochloride* be substituted for the ammonium sulphate trimethylamine is formed in both cases.—5. Trimethylamine hydrochloride does not act on formic aldehyde (Plöchl, *B.* 21, 2117).

Phenylhydrazide CH_2:$N_2HC_6H_5$ (?) [184°]. Colourless trimetric tables. Formed by adding phenyl-hydrazine to a solution of formic aldehyde (Wellington a. Tollens, *B.* 18, 3300).

Formic paraldehyde $(CH_2O)_3$? *Tri-oxy-methylene.* [152°].

Formation.—1. By spontaneous polymerisation of formic aldehyde in aqueous solution.—2. From methylene iodide by the action of Ag_2O or of silver oxalate. Also from methylene acetate by heating with water at 100° (Butlerow, *A.* 111, 242).—3. By heating calcium glycollate (1 pt.) with H_2SO_4 (7 pts.) at 175° (Heintz, *A.* 138, 43); and in small quantity by heating glycollic acid at 220° (Heintz, *J.* 1861, 444).—4. By the action of water on chloro- or di-chloro-dimethyl oxide ($MeO.CH_2Cl$ or $MeO.CHCl_2$) (Friedel, *C. R.* 84, 247; Butlerow, *Z.* 1865, 619).—5. By electrolysis of a solution of glycol, glycerin, mannite, or glucose in dilute H_2SO_4 (Renard, *A. Ch.* [5] 17, 303).

Properties.—Crystalline mass. Even below 100° it sublimes, but its melting-point is thereby raised from 152° to 172° (Tollens, *B.* 16, 919). Formic paraldehyde is converted on vaporisation into CH_2O (V.D. 1·06). It is insol. water, alcohol, and ether, but dissolves in cold aqueous NaOH or baryta. It is also dissolved by heating with water at 100°, being thereby converted into ordinary formic aldehyde (Tollens a. Mayer, *B.* 21, 1571). When hot it has a pungent odour. Heating with a trace of H_2SO_4 in a sealed tube at 115° converts it into '(*a*)-tri-oxy-methylene' $C_3H_6O_3$ [61°], V.D. 44·9 (H = 1); (*a*)-tri-oxy-methylene is sol. water, alcohol, and ether, and reduces ammoniacal $AgNO_3$ in presence of KOH (Pratesi, *G.* 14, 140). When a solution of formic aldehyde is evaporated over H_2SO_4 there is formed a soft substance, v. sol. water, whose molecular weight, determined by Raoult's method, corresponds to the formula $(CH_2O)_2$ (Tollens a. Mayer, *B.* 21, 3503).

Reactions.—1. PI_3 gives methylene iodide.—2. Boiling with alcohol and some H_2SO_4 gives $CH_2(OEt)_2$.—3. Boiling lime-water gives formose (methylenitan) (Butlerow, *A.* 120, 295).—4. Heating with water and MgO at 130°, and afterwards at 220°, gives formic acid and MeOH.—5. Ag_2O gives a silver mirror and formic acid (Heintz, *A.* 138, 322).—6. Conc. HClAq at 100° gives MeCl and formic acid (Tischtschenko, *J. R.* 15, 321).—7. Dry NH_3 forms hexamethylene-tetramine $C_6H_{12}N_4$, which crystallises from alcohol in rhombohedra; v. sol. water, sl. sol. cold alcohol, almost insol. ether (Butlerow, *A.* 115, 322).—8. *Ethylamine* gives $(CH_2)_2(NEt)_2$; di-ethylamine forms $CH_2(NEt_2)_2$; tri-ethylamine has no action. Other bases act in like manner when heated with formic paraldehyde (Ehrenberg, *J. pr.* [2] 36, 117).—9. *Chlorine* in sunlight forms $COCl_2$ and HCl (Tischtschenko, *J. R.* 1887, 479). *Bromine* gives $(CH_2Br)_2O$, formic acid, HBr, methyl bromide, CO, and CO_2.—10. $ZnEt_2$, followed by water, gives propyl alcohol. $ZnPr_2$ gives, in like manner, butyl alcohol (Tischtschenko, *Bl.* [2] 43, 112).—11. By heating with dilute HCl it is resolved into formic acid and MeOH or MeCl (T.). Dry HCl slowly forms $(CH_2Cl)_2O$ (102°-108°).—12. Dry HI is absorbed with formation of water and $(CH_2I)_2O$ (219°) (Tischtschenko, *J. R.* 1887, 464).—13. Dry HBr acts in like manner, forming $(CH_2Br)_2O$ (150°). This body is a pungent fuming oil, sol. ether, benzene, and acetone. Water decomposes it into Me_2O and HBr.—14. Aqueous HBr and formic paraldehyde at 140° give methyl bromide and formic acid.

Formic orthaldehyde $CH_2(OH)_2$.

Acetyl derivative $CH_2(OAc)_2$. *Methylene acetate.* (170°). Formed by the action of methylene iodide on silver acetate (Butlerow, *A.* 107, 111; 111, 242; Baeyer, *B.* 5, 1094; 6, 220). Formed also by treating $CH_2Cl.OAc$ with KOAc (Henry, *B.* 6, 739). Heavy liquid, sol. cold water, but when heated in a sealed tube for twenty hours at 100°, with a quantity of water insufficient to dissolve it in the cold, it is resolved into acetic acid and formic paraldehyde.

Acetyl derivative of the Methyl ether $CH_2(OMe)(OAc)$. (118°). From $CH_3.O.CH_2Cl$ and KOAc (Friedel, *B.* 10, 492). Decomposed by alkalis into water, HOAc, and formic paraldehyde.

Methyl ether $CH_2(OMe)_2$. *Methylene dimethyl di-oxide. Methylal.* Mol. w. 76. (42°). S.G. $\frac{20}{4}$ ·8604 (Brühl, *A.* 203, 12). *Critical temperature*: 224°. S. 28. H.C.p. 433,900 (Berthelot a. Ogier, *A. Ch.* [5] 23, 201). H.F.p. 88,210. H.F.v. 85,920 (*Th.*). Formed by distilling a mixture of water (3 pts.), H_2SO_4 (3 pts.), methyl alcohol (2 pts.), and MnO_2 (2 pts.) (Kane, *A.* 19, 175; Malaguti, *A.* 32, 55). Formed also by electrolysis of methyl alcohol (100 pts.) acidified with H_2SO_4 (1 pt.) diluted with water (4 pts.) (Renard, *A. Ch.* [5] 17, 291). Methylal is a liquid. A dose of 5g. to 8g. produces a hypnotic effect (Mairet a. Combemale, *C. R.* 104, 1022).

Reactions.—1. Methylal is employed by Baeyer (*B.* 5, 1094; 6, 220) as more convenient than formic aldehyde in obtaining derivatives of methane by elimination of water between that aldehyde and aromatic hydrocarbons. Thus, if a mixture of benzene (120 pts.), methylal (40 pts.), and acetic acid (400 pts.) be treated with a mixture of equal parts of HOAc and H_2SO_4 till the greater part of the benzene has separated, and the whole be then left for twenty-four hours, it will be found, after mixing with cold H_2SO_4 (2000 pts.), diluting after some hours with water, and shaking up with ether, that di-phenyl-methane has been formed: $CH_2(OMe)_2 + 2C_6H_6 = CH_2(C_6H_5)_2 + 2HOMe$. Methylal may serve as a nourishment for algæ; under these conditions they develop cellulose, but they only develop starch in daylight (Loew a. Bokorny, *J. pr.* [2] 36, 272).

Ethyl ether $CH_2(OEt)_2$. (89° cor.) (G.); (83°) (H.); (88°) (P.) S.G. $\frac{16·7}{16·7}$ ·826 (H.); $\frac{0}{}$ ·851 (G.); $\frac{0}{}$ ·840 (P.). V.D. 3·44 (H.). Prepared by the action of sodium on a solution of methylene chloride in absolute alcohol (Greene, *A. C. J.* 1, 522; *Bl.* [2] 45, 164; *C. R.* 89, 1077). Formed also by treating CH_2I_2 with NaOEt (Henry, *Bl.* [2] 45, 337; *C. R.* 101, 599); and by distilling formic paraldehyde with alcohol and a little H_2SO_4 (Pratesi, *G.* 13, 313). Mobile liquid, with agreeable odour like mint. Sl. sol. water, insol. conc. $CaCl_2Aq$.

Di-propyl ether $CH_2(OPr)_2$. (137°). S.G. $\underline{20}$ ·835 (Arnhold, *A.* 240, 199).

Di-isopropyl ether $CH_2(OPr)_2$. (118°). S.G. $\underline{20}$ ·831.

Di-isobutyl ether $CH_2(OCH_2Pr)_2$. (164°). S.G. $\underline{20}$ ·825.

Di-isoamyl ether $CH_2(OC_5H_{11})_2$. (207°). S.G. $\underline{20}$ ·835.

Di-octyl ether $CH_2(OC_8H_{17})_2$. (above 360°). S.G. $\underline{20}$ ·846

Di-benzyl ether $CH_2(OCH_2Ph)_2$. (above 360°). S.G. $\underline{20}$ 1·053.

Di-phenyl ether $CH_2(OPh)_2$. (299°). S.G. $\underline{20}$ 1·092.

Di-o-tolyl ether $CH_2(O.C_6H_4Me)_2$. [32°]. S.G. $\underline{50}$ 1·019. From methylene chloride and the sodium derivative of *o*-cresol (Arnhold, *A.* 240, 202).

Di-m-tolyl ether $CH_2(OC_6H_4Me)_2$. [45°]. (above 360°). S.G. $\underline{50}$ 1·052.

Di-p-tolyl ether $CH_2(OC_6H_4Me)_2$. [40°]. (above 360°). S.G. $\underline{50}$ 1·034.

Di-thymyl ether $CH_2(OC_{10}H_{13})_2$. [36°]. (above 360°). S.G. $\underline{50}$ ·979.

Formose $C_6H_{12}O_6$ dried at 90°. From formic aldehyde by adding cold milk of lime to a 4 p.c. solution, filtering, and leaving the filtrate to stand for some days (Loew, *J. pr.* [2] 33, 328).

Properties.—Syrup, sl. sol. alcohol, insol. ether. Sweet taste. ·055 g. reduce 10 c.c. of Fehling's solution. By heating at 100°–120° for five days it becomes 'methylenitan' $C_6H_{10}O_5$, which has a bitter taste, and has only one-fourth its reducing power. Prevents the precipitation of cupric sulphate by potash. Hot conc. HCl turns it brown, as it does cane-sugar and levulose, but not glucose; the filtrate can reduce Fehling's solution (Wehmer, *B.* 20, 2614). Cold milk of lime slowly destroys it. Warm alkaline solutions of picric acid are turned red, and indigo is bleached, as by glucose and levulose. Warmed with conc. alcoholic resorcin and HCl a ruby-red colour is produced; cane-sugar, levulose and glucose give paler colours (Ihl a. Pechmann, *C. C.* 1885, 761). Aqueous pyrogallol and HCl act similarly. Conc. alcoholic diphenylamine and HCl give a brownish-violet colour on warming. Schiff's reaction gives no colour with formose. Formose can undergo lactic but not alcoholic fermentation. It is, however, accompanied by a sugar that can undergo alcoholic fermentation (Loew, *B.* 22, 470). Alkaline diazobenzene sulphonic acid gives a red colour, as with carbohydrates and aldehydes. Phenyl hydrazine reacts thus: $C_6H_{12}O_6 + 2N_2H_3Ph = C_{18}H_{22}N_4O_4 + 3H_2O$. The product crystallises from dilute alcohol in slender needles. Plants which readily produce starch from glucose, cane-sugar, mannite, and glycerin do not produce it from formose (W.). When a solution of formose (10 g.) in water (1 litre) is boiled for a long time, the product extracted with chloroform, and the residue after evaporation of the chloroform treated with alcohol, aniline, and a little HCl, an intense red colour characteristic of furfurol is produced. This reaction is characteristic of sugars. In fact, when formose is digested with 1 p.c. sulphuric acid at 100°, more furfurol is formed than from other sugars (Loew, *B.* 20, 3039). Loew maintains that formose is well characterised as a sugar. E. Fischer (*B.* 21, 991) points out that the product of the action of lime-water on formic aldehyde is a mixture of three or more aldehydic or ketonic alcohols, one of them being the artificial sugar from acroleïn, acrose, characterised by its phenyl-hydrazide [217°] (Fischer a. Passmore, *B.* 22, 359).

Methylenitan $C_6H_{10}O_5$ (?). Obtained by the action of lime water on formic aldehyde or paraldehyde (Butlerow, *A.* 120, 296; *C. R.* 53, 145; Loew, *J. pr.* [2] 33, 321; 37, 203; Wehmer a. Tollens, *A.* 243, 340). The product is saturated with CO_2, filtered, and evaporated. Formed also by the action of heat upon formose. Amorphous gummy mass. Has a bitter taste. Does not react with phenyl-hydrazine. Sol. alcohol. When boiled with Fehling's solution it reduces only one-fourth as much CuO as glucose does. After boiling with dilute acids the reducing power is the same. It is optically inactive. It does not undergo alcoholic fermentation. When boiled for a long time with dilute H_2SO_4 it gives formic and acetic, but no levulic acids. It has no action on cold $CaCO_3$, but dissolves it and gives off CO_2 on heating. According to Loew (*J. pr.* [2] 33, 342), methylenitan $C_6H_{10}O_5$ is the saccharin of formose, and may be got by heating formose with lime or baryta and water at 70°–100°.

Pseudoformose. Got by boiling formic aldehyde in ·7 p.c. solution with tin (Loew, *J. pr.* [2] 34, 51). Resembles formose in most respects. Differs from formose (1) in giving orange, not violet, colouration, with resorcin, HCl, and alcohol; (2) 10 c.c. Fehling reduce ·052g.; (3) in forming the phenyl-hydrazine compound more quickly. Phenyl-hydrazine forms an osazone [123°]; when this body is heated for 30 hours in alcoholic solution at 100° its melting-point is found to have risen to 148°.

(β)-Formose. Formed when a ·1 p.c. solution of formic aldehyde is boiled for 5 hours with much tin (Loew, *B.* 21, 270). Thick, sweet, non-fermentable syrup; does not become brown at 100°. It yields humous substances with HCl. Turned brown by potash. Its solution in alcoholic HCl yields a wine-red colour with resorcin and a steel-blue colour with diphenylamine. 10 c.c. of Fehling's solution are reduced by ·0739 of (β)-formose. Its phenyl-hydrazide or 'osazone' $C_{18}H_{22}N_4O_4$ crystallises in small yellow needles [148°].

Two other formoses or non-fermentable sugars are said by Loew to be formed by heating formic aldehyde, 3 pts., at 100° with an aqueous solution (1000 pts.) of magnesia obtained by treating a 7 p.c. solution of $MgSO_4$ with litharge. One of these gives with phenyl hydrazine an osazone crystallising from benzene in yellow needles [152°].

Isomeride of Formose (?). In the electrolysis of glycerin (30 vols.) acidified with H_2SO_4 (2 vols.), diluted with water (20 vols.), there is formed, together with formic paraldehyde, a syrupy isomeride of formic aldehyde. It blackens at 90°, giving an odour of burnt sugar. It is v. e. sol. alcohol and water, is unfermentable, reduces Fehling's solution and ammoniacal $AgNO_3$. Its solution is ppd. by ammoniacal lead acetate but not by lead subacetate. HNO_3 oxidises it to oxalic acid. Baryta added to its alcoholic solu tion ppts. $(C_6H_{12}O_6)_4 3BaO$. This body is perhaps identical with formose or methylenitan.

FORM-IMID-AMIDE *v.* FORMAMIDINE.

Form-ethyl-imid-ethyl-amide *v.* *s*-DI-ETHYL-FORMAMIDINE.

FORM-IMID-DI-ETHYL-AMIDE *v.* *u*-DI-ETHYL FORMAMIDINE.

FORM-IMIDO-ETHER C_3H_7NO *i.e.* NH:CH.OEt. (80°)? Hydrochloride B'HCl. Formed by the action of gaseous HCl (2 mols.) on dry HCy (1 mol.) mixed with alcohol (1 mol.) in a freezing mixture (Pinner, *B.* 16, 354, 1644). Glittering prisms. Very unstable, decomposing on keeping with formation of NH_4Cl. With alcohol it gives NH_4Cl and orthoformic ether.

Reactions.—1. Decomposed by heat into EtCl, formic ether, and the hydrochloride of formamidine.—2. KOH separates a small quantity of an oil (80°).—3. Alcoholic NH_3 in the cold gives formamidine.—4. Dimethylamine forms $NH:CH.NMe_2$.—5. Methyl-aniline forms $C_6H_5NMe(CHO)$.—6. Phenyl-hydrazine forms $C_{13}H_{14}N_4$.—7. An alcoholic solution of NEt_2H slowly forms a base $C_{10}H_{21}N_3$ which forms a platinochloride $B'_2H_2PtCl_6$ [153°] crystallising in flat prisms (Pinner, *B.* 16, 1650; 17, 180).—8. NaOAc and Ac_2O give NH:CH.OAc [70°] which crystallises from ether in short prisms, v. sol. ordinary menstrua.

Formimido-methylene ether $(NH:CHO)_2CH_2$. Hydrochloride B''2HCl. Formed by passing HCl into glycol (1 mol.) and HCy (2 mols.) diluted with ether at 0° (Pinner).

FORMINS. Formyl derivatives of polyhydric alcohols. They are described under the alcohols from which they are derived.

FORM-METHYL-IMID-METHYL-AMIDE *v.* DI-METHYL-FORMAMIDINE.

FORMO-CUMIDIDE *v.* CUMIDINE. Formyl derivatives of bases are described for the most part both under FORMIC ACID and under the bases.

FORMOGUANAMINE $C_3H_5N_5$. [above 350°]. Formed together with CO_2, ammonia, CO, and water by heating guanidine formate at 200° (Nencki, *B.* 7, 1584). Trimetric needles, with feeble alkaline reaction. V. sol. hot water, sl. sol. alcohol. May be sublimed with partial carbonisation.—B'HCl: trimetric plates. — $B'_2H_2PtCl_6$.—$B'HNO_3$: needles or prisms.—$B'H_2C_2O_4$: granular-crystalline pp., insol. cold, sl. sol. hot, water.

FORMO-NAPHTHALIDE *v.* *Formyl derivative* of NAPHTHYLAMINE.

FORMOSE *v.* FORMIC ALDEHYDE.

FORMO-TOLUIDE *v.* *Formyl derivative* of TOLUIDINE.

FORM-PHENYL-IMID-PHENYL-AMIDE *v.* DI-PHENYL-FORMAMIDINE.

FORMULÆ. Symbols have been in use in chemistry from the earliest period of the science, but as knowledge has grown their meaning has become deeper and deeper; and the difference between the significance of the earliest symbols and of the elaborate chemical formulæ of the present is as great as the difference between the knowledge of chemical phenomena possessed by the earliest chemists, and that possessed by the chemists of to-day. The first attempt of any importance to represent more than the name of a substance was that of Hassengratz and Adel in 1787. These chemists represented all metals by circles, in which were written the first letters of the Latin names thus: Copper Ⓒ, lead Ⓟ. All alkalis and alkaline earths were represented by triangles placed in different positions; oxygen by a horizontal line, &c., &c. The composition of compound substances was represented by placing side by side the symbols of the elementary substances contained in them. This system was recommended by Lavoisier, Berthollet, and Fourcroy in a report made by them to the French Academy in 1787, but it was not generally accepted. The next suggestion of importance was made by Dalton in 1808. He represented the atoms of the elements by circles, and distinguished them by various additions. Thus, hydrogen was represented by ⊙, oxygen by ○, nitrogen by ⦶, sulphur by ⊕, &c. The composition of compounds was represented by placing side by side the symbols of the elements of which the compounds were made up. Thus, water was represented by the symbol ⊙○, ammonia by ⦶⊙, nitrous oxide by ⦶○⦶, &c. The present system of symbols was introduced by Berzelius. They are based upon the atomic theory, each symbol of an element being intended to represent an atom of an element. As is well known, the symbol of an element is the first letter, or the first letter and some other letter, of the name of the element. In many cases the symbol is derived from the Latin name of the element.

The composition of compounds was represented by writing side by side the symbols of the elements which were in combination. The symbol of a compound was thus an expression of the view held regarding the structure of the compound. As H represents an atom of hydrogen and O an atom of oxygen, the symbol HO for water meant that what was then called an atom of water was made up of an atom of hydrogen and an atom of oxygen. So far as it represented that water is made up of hydrogen and oxygen in the proportion by weight of 1 pt. of the former to 8 pts. of the latter, it represented a fact in regard to which there could be no dispute. But when it was interpreted as meaning that an atom of hydrogen is in combination with an atom of oxygen, a definite theory in regard to the structure of matter was involved. The difficulties in the way of determining atomic weights have been referred to in previous articles (*v.* ATOMIC AND MOLECULAR WEIGHTS, vol. i.). Until the introduction of the method of Avogadro, and that of Dulong and Petit, for the determination of atomic weights, there was much difference of opinion in regard to the figures to be adopted, and, therefore, the symbols did not always represent the same thing. At the present time most chemists are agreed as to the system of atomic weights, and the symbols of the elements now in use are intended to represent atomic weights as determined mainly by the methods of Avogadro, and Dulong and Petit. These atomic weights are strongly confirmed by the discovery of the periodic law, which would be meaningless with any other system than that now generally adopted. There are some chemists in France who refuse to accept the atomic weights, and the symbols used by them do not mean the same thing as those used by other chemists.

The chemical formula of a compound is intended primarily to represent the quantitative composition of the compound. In terms of the accepted theory of the structure of matter, it is intended to tell what atoms, and how many, are combined to make the smallest particle of the compound which exhibits the properties of that compound. This smallest particle of the compound is called a molecule. The formula then is intended to represent a molecule. In the case of gaseous compounds, or of compounds which can be converted into gases without undergoing decomposition, we have, of course, the means of determining the relative weights of the molecules on the basis of Avogadro's law. The methods, then, which are involved in the determination of molecular formulæ are these: (1) the substance must be analysed; (2) the molecular weight must be determined. The formula must express the results of both determinations. To show how this is done one example will suffice. Let it be desired to determine the molecular formula of water. The analysis shows that it consists of hydrogen and oxygen in the proportion of 1 pt. by weight of the former to 8 pts. by weight of the latter. This is a fact involving no speculation whatever, and any formula adopted must be in accordance with this fact. The next step is to determine the specific gravity of water vapour. As compared with air its specific gravity is 0·623. This gives the relative weight of the molecule of water, and, adopting the usual standard, it shows the molecular weight of water to be 18. The atomic weight of oxygen has been shown to be 16, if that of hydrogen is 1, so that we now have all the data for writing the molecular formula. A molecule which consists of hydrogen and oxygen in the proportions mentioned above, and the weight of which is 18 in terms of an accepted unit weight, must contain 2 atoms of hydrogen and 1 atom of oxygen. This is expressed by the formula H_2O. A molecule thus made up weighs 18 times as much as an atom of hydrogen, or the molecular weight of the compound is 18, the 18 pts. being made up of 16 pts. of oxygen and 2 pts. of hydrogen. Thus the formula expresses the results of the analysis and of the determination of the specific gravity of water vapour, and these results are interpreted in terms of the molecular and atomic theory and the law of Avogadro. This is true of every formula of a gaseous substance.

As regards the molecular formulæ of liquid and solid substances we know but little. Many facts indicate that the molecules of liquids and solids are much more complex than those of gases, but no altogether satisfactory method has yet been discovered for determining the molecular weights of such substances. Among the facts which lead to the conclusion that the molecules of liquids and solids are complex may be mentioned, the not uncommon observation that just above the boiling-point vapours have a greater specific gravity than at a higher temperature. It is not probable that the molecules of liquid and solid sulphur contain less than six atoms. The existence of allotropic modifications of the solid elements sulphur and phosphorus is probably best explained by assuming that the molecules of the allotropic modifications contain different numbers of atoms.

An attempt has been made to establish a method for the determination of the molecular weights of solids by means of observations upon the freezing-points of solutions. Many observations have shown that there is a definite connexion between the molecular weights of solids and the freezing-points of their solutions, and the law expressing this connexion has been stated provisionally by Raoult, who finds that quantities of chemically similar compounds proportional to the molecular weights of these compounds generally produce equal lowerings of the freezing-points of water and other solvents. There seem, however, to be exceptions to this law.

The formulæ of liquids and solids are not molecular formulæ in the sense in which the formula of a gas of which the specific gravity is known is. Even the formula of water H_2O is strictly applicable only to water in the state of vapour. Whether on condensing to the form of the liquid several of the simple molecules unite to form more complex molecules, we cannot positively say, but probably they do. So also, when the liquid water becomes solid ice, it is not improbable that a still further union of molecules takes place.

If we consider the case of a solid compound which cannot be converted into vapour, our formula plainly cannot express the molecular weight at all. In writing the formula of sodium chloride NaCl, we do so because that is the simplest formula which will express the fact that the compound consists of 23 pts. of sodium and 35·5 pts. of chlorine. But the formulæ Na_2Cl_2, Na_3Cl_3, Na_4Cl_4, &c., express the results of analyses just as well, and at the same time are probably nearer the truth than the simpler one. The time may come when it will be necessary to express the molecular weights of solids and liquids, as well as of gases, in chemical formulæ. At present, so far as the facts which we generally have to express in our formulæ are concerned, it is not a matter of any special importance whether we know the true molecular weights or not. Indeed, it is not improbable that, even though the molecules of solids and liquids are comparatively complex, they are reduced to the simple forms under the conditions under which chemical action takes place. Thus, when a solid or a liquid is dissolved, probably the complex molecules of which it is composed are broken down and become simple in the dilute solutions. This would be in accordance with the fact that solutions act readily upon one another; and it is in accordance with recent work on the electrolytic conduction of salts in solution (*v.* PHYSICAL METHODS).

From what has been said it is clear that we have to distinguish between *molecular formulæ* and *composition-formulæ*, the former being applicable only in cases of gases, the latter being used in cases in which molecular formulæ cannot be written owing to a lack of knowledge of the facts. In both these kinds of formulæ the atomic theory is involved.

But chemists have come to express much more by their formulæ than the composition and the molecular weights of compounds. They express views in regard to the arrangement or relations of the parts which are in combination. Neither the atomic theory nor the hypothesis of

Avogadro has any direct connexion with the arrangement of the parts constituting a molecule. All that the former claims is that, when chemical action takes place, it takes place between certain minute particles called atoms; that when an act of chemical combination occurs two or more atoms combine. The hypothesis of Avogadro goes one step further. According to it the particles formed by the combination of atoms, *i.e.* the molecules, bear such relations to one another that they always require the same space for the same number, no matter what their composition may be.

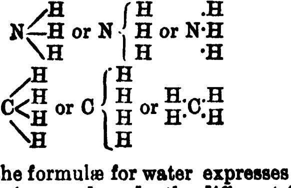
As a result of the study of the chemical changes of compounds, however, chemists have come to hold certain views in regard to the relations of the parts, or atoms, which enter into the composition of molecules. Formulæ which express these views are called in general *rational formulæ*, or *constitutional* or *structural formulæ*. Rational formulæ have been in use in chemistry for a long time. Lavoisier's studies on oxygen and the phenomena of combustion led him to ascribe to that element a degree of supreme importance. According to him the oxygen was the chief constituent of every compound. It was oxygen which made acids what they are, and oxygen which made bases what they are. When a salt is formed the acid and base unite, and the salt consists of the two parts in combination. Thus potassium nitrate is $KO.NO_5$, sodium sulphate $NaO.SO_3$, &c. These formulæ not only express the composition of the compounds which they represent, they express the view that the salts consist of two parts, each of which contains oxygen. The same view was extended to other compounds, and the attempt was made to express the constitution of every compound in a similar way. The constitutional formulæ thus introduced were based upon the hypothesis of *dualism*. They were called *dualistic formulæ*. The dualistic view found support in a study of the action of the electric current on chemical compounds. As compounds are decomposed by the electric current into two parts, one going to the positive, the other to the negative, pole, the view that every compound consists of two parts was thus plainly strengthened. The introduction of the electro-chemical theory by Berzelius led to the general use of dualistic formulæ. These formulæ were intended to represent the electro-negative and the electro-positive constituent of each compound. For a long time these formulæ were used exclusively, and in some books even at the present day they are found, though many facts have been discovered which show that the electro-chemical theory is untenable—at least, in the form in which it was put forward by Berzelius (*v.* DUALISM).

Owing to the complexity of the compounds of carbon, and the fact that they readily undergo changes, the chief studies which have led to the views at present held have been made with regard to these compounds. At one time what was called the *theory of radicles* played an important part, and at this time every formula expressed the views of chemists regarding the particular radicle or radicles contained in a compound. These radicles were groups of atoms which could be transferred from one compound to another without undergoing change of composition. According to the *theory of conjugate compounds* (*Theorie der gepaarten Verbindungen*), every complex compound is made up of some simple compound conjugated with a complex group. Thus aniline was regarded as made up of ammonia conjugated with a group C_6H_4, as represented in the formula $C_6H_4.NH_3$. The sulphonic acids were in the same way regarded as made up of sulphuric acid conjugated with various groups of carbon and hydrogen. Next came the *theory of types*, which regards all compounds as built according to a few plans. The general plans of all compounds were found in simple compounds like hydrochloric acid, water, ammonia, and marsh gas. In saying that alcohol, for example, belongs to the water type it was meant that it may be regarded as derived from water by the substitution of the group C_2H_5 for a part of the hydrogen in water. The relation between the two was represented by the formulæ $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ and $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$. So, too, aniline was regarded as belonging to the ammonia type, and the relation between them was represented by the formulæ $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$ and $\left.\begin{matrix}C_6H_5\\H\\H\end{matrix}\right\}N$. It will be seen that this method of classification or of expressing constitution involves the conception of substitution and, to some extent, the conception of radicles *i.e.* of complex groups playing the part of single atoms. The object of a typical formula was to show to which of the types a compound was related, and in what way it was regarded as derived from the type. It was found necessary to refer many compounds to more than one type, and this led to what was called the *theory of mixed types*. The compound methylamine may serve to illustrate this. It may be regarded as derived from ammonia, in which case it must be represented by the formula $\left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}N$, or it may with equal right be regarded as derived from marsh gas, and it must then be represented by the formula $\left.\begin{matrix}NH_2\\H\\H\\H\end{matrix}\right\}C$. Both these views may, however, be harmonised, and the compound represented as belonging to both types thus

$$N\left\{\begin{matrix}H\\H\\\left.\begin{matrix}H\\H\\H\end{matrix}\right\}C.\end{matrix}\right.$$

It is thus seen that chemists for more than a century have attempted by means of formulæ to express their views in regard to the constitution of chemical compounds in terms of prevailing hypotheses. But the formulæ thus framed were in most cases more than mere expressions of theory. They attempted to express certain facts that were known. In the dualistic formulæ the fact was expressed that compounds are formed by the union of two parts. In the electro-chemical formulæ the fact was expressed that compounds break down into two parts under the influence of an electric current. In the formulæ representing conjugate compounds, the fact that some of the compounds thus represented have properties highly suggestive of the fundamental substance supposed to be contained in them was recognised; and in the typical formulæ the fact that the general conduct of the compound represented is like that of the type to which it is regarded as belonging is intended to be expressed. When alcohol is represented as belonging to the water type, for example, the chemical conduct of the two substances is the justification for the view expressed. All the constitutional formulæ, then, are intended to express facts established by study of the compounds. Everything learned in regard to a compound must be in accordance with the formula, and must, if possible, find an interpretation in the formula. It would be absurd, for example, to represent a marked acid as belonging to the ammonia type, unless it could be shown that, together with its acid properties, the compound also has certain properties which suggest those of ammonia.

Let us now consider the constitutional formulæ used by most chemists of the present day. These, like all preceding constitutional formulæ, are intended to express the facts in terms of the prevailing hypotheses. The type theory gave way to the valency hypothesis which was first suggested by Frankland and afterwards elaborated by Kekulé, Couper, Kolbe and others. According to this the cause of the types is to be looked for in the atoms of which the typical compounds are made up. Atoms differ from one another in the number of other atoms which they can hold in combination at the same time. The so-called types are simply representative compounds, illustrating the forms of compounds possible in the case of monovalent, divalent, trivalent, and tetravalent, elements. Just as the atom of hydrogen is in combination with chlorine in hydrochloric acid, so each atom of hydrogen is in combination with oxygen in water, with nitrogen in ammonia, and with carbon in marsh gas. This view involves the conception of the *linkage of atoms*. Instead of conceiving each molecule of water, of ammonia, and of marsh gas, as made up of a certain number of atoms all in direct combination, we now conceive that in these molecules there are direct connexions between some of the atoms and not between others. While in the molecules named the hydrogen is in direct combination with oxygen, with nitrogen, and with carbon, it is not believed to be in direct combination with hydrogen. These views are expressed by the following formulæ:—



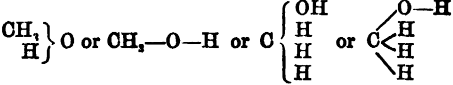
$$\mathrm{H{-}O{-}H}\ \text{or}\ \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\ \text{or}\ \mathrm{H.O.H}$$

$$\mathrm{N}\begin{matrix}\diagup\mathrm{H}\\{-}\mathrm{H}\\\diagdown\mathrm{H}\end{matrix}\ \text{or}\ \mathrm{N}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right.\ \text{or}\ \mathrm{N}\begin{matrix}.\mathrm{H}\\\cdot\mathrm{H}\\\cdot\mathrm{H}\end{matrix}$$

$$\mathrm{C}\begin{matrix}\diagup\mathrm{H}\\{<}\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\\\diagdown\mathrm{H}\end{matrix}\ \text{or}\ \mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right.\ \text{or}\ \begin{matrix}\mathrm{H.}\\\mathrm{H\cdot}\end{matrix}\mathrm{C}\begin{matrix}\mathrm{.H}\\\mathrm{\cdot H}\end{matrix}$$

Each of the formulæ for water expresses exactly the same view, and so do the different formulæ for ammonia and for marsh gas. The facts which lead to the acceptance of the valency hypothesis have been considered pretty fully in the article EQUIVALENCY (*q. v.*) and they need not be repeated here. Suffice it to say that the evidence in favour of the view that there are definite lines of connexion between the different parts of molecules is extremely strong, and that without this view it appears to be impossible to explain the many cases of isomerism which present themselves in the field of organic chemistry. In our constitutional formulæ at present we endeavour to state what lines of connexion exist in the molecules. These formulæ are based upon the molecular and atomic theory, the hypothesis of the linkage of atoms, and to some extent upon the valency hypothesis.

The difference between a *typical formula* and a *linkage-formula* is very slight in simple compounds, and when the linkage-formula is written without the use of lines or points to indicate the connexions between the atoms, it is identical in appearance with the typical formula. It is nevertheless intended to express something which the typical formula did not express. We may write methyl alcohol:—



$$\left.\begin{matrix}\mathrm{CH_3}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\ \text{or}\ \mathrm{CH_3{-}O{-}H}\ \text{or}\ \mathrm{C}\left\{\begin{matrix}\mathrm{OH}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right.\ \text{or}\ \mathrm{C}\begin{matrix}\diagup\mathrm{O{-}H}\\{<}\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\\\diagdown\mathrm{H}\end{matrix}$$

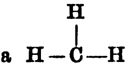
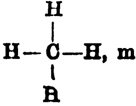
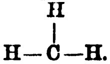
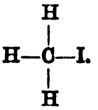
Each formula is intended to express exactly the same thing, and that is, that of the four hydrogen atoms contained in the molecule of methyl alcohol, three are in direct combination with carbon alone, and one with oxygen; while the oxygen is in direct combination with carbon as well as with hydrogen. The formulæ also express the relation between water and methyl alcohol, but that fact is not regarded as the principal one, as it was when the theory of types was the controlling idea. While it is not difficult to see how by means of such formulæ it is possible to express the constitution of compounds, it is not so easy to see how, when more than one formula is possible for the same compound, the selection is made. It is thought by some that, in order to express the constitution of a compound, it is only necessary to know the valencies of the atoms which form the molecule of the compound, and to arrange these atoms in such a way as to satisfy all the hypothetical affinities or bonds. Thus the constitution of sulphuric acid is written $\mathrm{S}{<}\begin{matrix}\mathrm{O{-}O{-}H}\\\mathrm{O{-}O{-}H}\end{matrix}$ by some, because sulphur and oxygen are divalent and hydrogen is monovalent. In this case to be sure there are two other ways in which the constitutional formula may be written on the above assumptions. They are $\mathrm{H{-}O{-}S{-}O{-}O{-}O{-}H}$ and $\mathrm{H{-}S{-}O{-}O{-}O{-}O{-}H}$. Such formulæ, however, are conventional methods of expressing certain matters which call for evidence. They are simply the results of the application of the hypothesis of valency and express something in regard to which we know nothing until the subject has been investigated. Who, for example, can tell without investigation whether in sulphuric acid both hydrogen atoms are in combination with oxygen, or whether one is in combination with oxygen and the other with sulphur? One view is just as probable *a priori* as the other, and there is nothing in the hypothesis which will enable us to decide between them. And so in most other cases. The hypothesis of the linkage of atoms affords us a ready method of expressing facts which are known to us, but it does not furnish us with the facts. What kinds of facts then can be expressed by means of the hypothesis, and how can we become acquainted with these facts?

Answers to these questions will best be given by means of examples. There are two compounds known which by the usual methods can easily be shown to have the molecular formula C_2H_3N. Without further information, any attempt to express views in regard to the structure of these substances would be mere speculation. By studying the chemical conduct of both we soon recognise marked differences between them. One of them shows a tendency to decompose in such a way that the nitrogen is given off in the form of ammonia, while the two carbon atoms remain. Thus, under proper conditions this decomposition takes place:

$$C_2H_3N + 2H_2O = C_2H_4O_2 + NH_3.$$

The other compound breaks down in an entirely different way, the nitrogen remaining in combination with one of the carbon atoms, and the other carbon atom being given off thus:

$$C_2H_3N + 2H_2O = CH_5N + H_2CO_2.$$

These facts suggest that the carbon and nitrogen in these two compounds are held together in different ways. In the first it appears probable that the connexion is as represented in the formula C—C—N; while in the second it appears that the connexion is this, C—N—C. As regards the way in which the hydrogen atoms are held in combination, it can be shown that the compounds formed by decomposition of the two bodies under consideration contain the methyl group CH_3, which, from its formation from marsh gas, is easily shown to have the constitution represented by the formula  $H-\overset{\overset{H}{|}}{C}-H$; or, to be more strictly accurate, the formation from marsh gas shows that if marsh gas has the formula  $H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$, methyl is  $H-\overset{\overset{H}{|}}{C}-H$. As the valency of the carbon atom is never greater than four, so far as is known, it appears that the first of the two compounds has the constitution H_3C—C—N, and the other the constitution H_3C—N—C. These formulæ are in accordance with the decompositions above mentioned, and they suggest the conduct of the substances. Again, the methods of formation of the substances confirm the conclusions already drawn in regard to their constitution. Both are formed when a salt of hydrocyanic acid is treated with a mono-halogen derivative of marsh gas such as methyl iodide CH_3I. According to the prevailing notions, for which there is abundant evidence, methyl iodide is marsh gas in which one atom of hydrogen has been replaced by one atom of iodine. Its constitution is therefore represented thus:  $H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-I$. When this is treated with silver cyanide the silver and iodine unite and the residue of marsh gas, *i.e.* methyl, CH_3, unites with the cyanogen. Thus a compound is formed which is represented by the formula $H_3C(CN)$. And, just as the silver salt is called silver cyanide, so this compound would naturally be called methyl cyanide. But, as already stated, there are two compounds formed. One is called *methyl cyanide*, and the other *methyl isocyanide.* While the method of formation plainly indicates the presence of methyl in both compounds, it does not give any clue to the way in which the carbon and nitrogen of the cyanogen are united with the methyl. According to all we know concerning carbon and nitrogen, either may act as a linking element, so that the two possibilities suggest themselves which are represented by these formulæ, H_3C—C—N and H_3C—N—C. We do not know whether silver cyanide has the structure Ag--C—N or Ag—N—C; as both the methyl compounds mentioned are formed by treating silver cyanide with methyl iodide, it seems not improbable that the salt contains both varieties. However this may be, it is clear that the method of formation of the methyl compounds does not afford us any clue to the structure of the cyanogen group. Our information in regard to this is obtained solely by a study of the decompositions of the compounds.

For the two formulæ under discussion we have experimental evidence, and the formulæ express the results of experiments. These results are interpreted in terms of the linkage-hypothesis. So far these formulæ are practically independent of the hypothesis of valency. The conception that the molecule of marsh gas consists of one carbon atom in combination with four hydrogen atoms is a necessary consequence of the view that the molecule is symmetrical, and this view is entirely in accordance with all facts known regarding the compound. This conception is not perhaps so much a result of the application of the hypothesis of valency, as of our knowledge of the conduct of marsh gas. On now examining the formulæ for methyl cyanide and methyl isocyanide in the light of the hypothesis of valency, we see that in that of methyl cyanide, H_3C—C—N, one carbon atom is represented as tetravalent, the other as divalent, and the nitrogen as monovalent. In the formula of the isocyanide, H_3C—N—C, one carbon atom appears to be tetravalent, one monovalent, and the nitrogen divalent. But, as in most compounds carbon is tetravalent and nitrogen either trivalent or pentavalent, it is generally held that in these compounds they also act in this way, and the formulæ are written so as to indicate this. Methyl cyanide is represented thus $H_3C—C\equiv N$, and the isocyanide thus $H_3C—N\equiv C$, the nitrogen being trivalent in the former and pentavalent in the latter. It will be seen that the chief reason for writing the formulæ in this way is to account for the distribution of the hypothetical bonds or affinities. No experimental evidence has been furnished in favour of these formulæ, and, so far as our knowledge of facts is concerned, the simpler formulæ represent just as much as the more complex ones.

The two examples discussed will give a fair idea of the methods in use for determining the structure or constitution of compounds and of expressing the results by means of formulæ. The results reached by a study of the reactions of a compound are expressed by means of a *reaction-formula*. Those reached by a study of the method of synthesis of a compound are expressed by means of a *synthesis-formula*. As it is found that in most cases the reaction-formula is identical with the synthesis-formula, the expression is called a *structural* or *constitutional formula*. The structure or constitution may be expressed by means of a simple *linkage-formula* in which the connexions between the atoms as determined by experiments are pointed out; or a *valency-formula* in which an attempt is made to express different kinds of connexions between atoms. The linkage-formula is based upon experiments; the valency-formula, so far as it expresses more than the linkage-formula, is almost wholly an expression of an hypothesis.

The constitutional formulæ of all the great groups of chemical compounds have been determined by experiments, and they are of great value in enabling chemists to express very concisely in intelligible language the results of experiments. As it is found that a certain kind of constitution carries with it a certain set of properties, the formula conveys to the mind at once a clear impression in regard to the general properties of the compound represented. It has been shown by experiment that in every alcohol hydrogen is linked to oxygen, and the group thus formed, which is called hydroxyl, is in turn linked to a hydrocarbon residue. Methyl alcohol, for example, is represented thus $H_3C—O—H$. Now, whenever we see an expression of this kind $R—O—H$, in which R is any hydrocarbon residue, we may expect that the substance thus represented has certain general properties which are characteristic of all alcohols. The analogy between these substances and water and the metallic bases is also clearly indicated by their formulæ. Thus we have this series:—

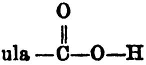
$H—O—H$ water,
$K—O—H$ potassium hydroxide,
$Na—O—H$ sodium hydroxide,
$M—O—H$ any hydroxide of a monovalent metal,
$H_3C—O—H$ methyl alcohol,
$H_5C_2—O—H$ ethyl alcohol,
$R—O—H$ any alcohol containing a monovalent residue of a hydrocarbon.

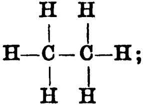
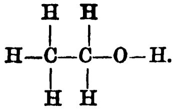
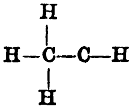
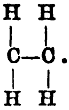
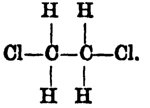
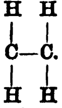
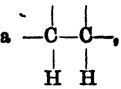
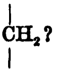
A very interesting piece of evidence in favour of the linking represented in these formulæ is furnished by the action of a reagent which has the power of removing oxygen and putting chlorine in its place. Such a reagent is pentachloride of phosphorus, PCl_5. When it is brought in contact with a substance containing oxygen this element is abstracted and two chlorine atoms from the pentachloride take the place of each atom of oxygen. If the oxygen serves the purpose of a linking element, as it does in the compounds above represented, the compound breaks down in such a way that the parts linked together by the oxygen appear in separate molecules. Thus, replacing the oxygen in the above compounds by chlorine, we should have this series:—

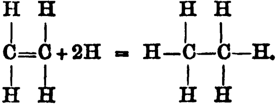
$H—Cl$	$Cl—H$
$K—Cl$	$Cl—H$
$Na—Cl$	$Cl—H$
$M—Cl$	$Cl—H$
$H_3C—Cl$	$Cl—H$
$H_5C_2—Cl$	$Cl—H$
$R—Cl$	$Cl—H$

In each case decomposition takes place, and two molecules are formed from one. The general reaction in the case of metallic hydroxides is: $M—O—H + PCl_5 = POCl_3 + MCl + HCl$; and in the case of alcohols it is:

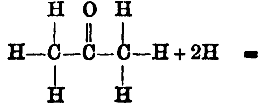
$$R—O—H + PCl_5 = POCl_3 + RCl + HCl.$$

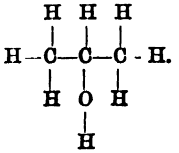
It is evident that oxygen has some power which chlorine does not possess. It can link together hydrogen and another element, while in the cases mentioned chlorine cannot. In a similar way an elaborate study of acids has shown that in most of them the hydrogen which is replaceable by metallic elements is in combination in the form of hydroxyl, but the hydroxyl instead of being in direct combination with a metal, as in the hydroxides above referred to, is generally in combination with some element which is in turn in combination with oxygen. The constitution of nitric acid, for example, has been found to be probably represented thus $O_2N—O—H$; sulphuric acid thus $O_2S{<}^{O—H}_{O—H}$; permanganic acid thus $O_3Mn—O—H$; chromic acid thus $O_2Cr{<}^{OH}_{OH}$, &c., &c. So too the carbonates are found to be derived from an acid which probably has the structure represented by the formula $OC{<}^{OH}_{OH}$. On studying the acids of carbon, or the so-called organic acids, most of them are found to contain hydroxyl in combination with carbonyl, forming together the group known as carboxyl which has the structure $OC—O—H$. The greater number of the monobasic carbon acids may be represented thus $OC{<}^{R}_{OH}$ or $R.CO.OH$. These formulæ show the relations which exist between the acids in question and carbonic acid. If in the latter we suppose a hydroxyl group replaced by a residue like methyl, ethyl, &c., the result is a carbon acid or an organic acid. Acetic acid is $OC{<}^{CH_3}_{OH}$; propionic acid is $OC{<}^{C_2H_5}_{OH}$; or these formulæ may also be written $CH_3.CO.OH$ and $C_2H_5.CO.OH$ respectively. These are linkage-formulæ based upon experiments. If we write them thus $H_3C—\overset{O}{\overset{\|}{C}}—O—H$ and $H_5C_2—\overset{O}{\overset{\|}{C}}—O—H$, we then have to deal with valency-formulæ, and they, as already remarked, convey no more information than the linkage-formulæ, unless by further experiments we become acquainted with facts which justify us in expressing the relation between the hydroxylic oxygen and carbon in a different way from that in which we express the relation between the carbonylic oxygen and carbon. In this case we are certainly justified in making the distinction. It is found that when the oxygen of the hydroxyl is replaced by chlorine, one chlorine atom takes the place of the hydrogen and oxygen of the hydroxyl, and the other passes off in combination with hydrogen as hydrochloric acid. It appears therefore that but one chlorine atom can enter in the place formerly occupied by the hydroxylic oxygen. This is represented by the single line $C—O—H$. On the other hand, under a change of conditions, it is found possible to replace the carbonylic oxygen by chlorine, and in this case two chlorine atoms enter into the molecule in place of the oxygen. This we may represent by two lines thus, C=O. In this case then the formula  $\begin{array}{ccccc} & & O & & \\ & & \| & & \\ — & & C & —O— & H \end{array}$ is more than a mere application of the valency-hypothesis, it is the expression in a particular language of a number of facts, among which are some which justify the use of the double line, if that is used simply as an expression of the facts.

It is not the purpose of this article to show how the structural formulæ of all the different classes of compounds are deduced from experimentally determined facts, but rather to illustrate the general principles which are made use of, and to show in what way the formulæ express the facts. The question of single and double union has just been touched upon in connexion with the relations existing between carbon and oxygen. The same question has frequently been discussed with special reference to the relations between carbon atoms. A concrete case is that of ethylene. As is well known, this hydrocarbon has the molecular formula C_2H_4. It is obtained from ethane C_2H_6 by the indirect abstraction of two atoms of hydrogen, or from alcohol C_2H_5—O—H by the abstraction of the elements of water. In ethane it is assumed that the linkages occur as represented by the formula  $\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$; and in alcohol as represented by the formula,  $\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & — & C & — & C & — & O & — & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$.
Now when hydrogen is abstracted from ethane, or water from alcohol, the action may plainly take place in two ways so as to form a compound of the structure,  $\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & — & C & — & C & — & H \\ & & | & & & & \\ & & H & & & & \end{array}$, or one of the structure  $\begin{array}{ccc} H & & H \\ | & & | \\ C & — & C \\ | & & | \\ H & & H \end{array}$. But when ethylene is treated with chlorine a compound of the formula $C_2H_4Cl_2$ is formed, and it has been shown that in this compound each chlorine is in combination with a different atom, as represented in the formula  $\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ Cl & — & C & — & C & — & Cl \\ & & | & & | & & \\ & & H & & H & & \end{array}$. It appears from this that ethylene is, in all probability, made up as represented in the formula  $\begin{array}{ccc} H & & H \\ | & & | \\ C & — & C \\ | & & | \\ H & & H \end{array}$. So far this formula expresses all that we have learned, and it appears that, in ethylene, carbon is trivalent. But ethylene has a power which ethane has not. It can take up two atoms of hydrogen, of chlorine, bromine, &c. It is unsaturated. We may represent this fact by the formula  $\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ — & C & — & C & — \\ & | & & | & \\ & H & & H & \end{array}$, which, if interpreted in terms of the hypothesis of valency, means that two of the affinities of each carbon atom are employed in holding hydrogen in combination, one of each in holding the two carbon atoms together, and one of each is unemployed. There are several objections to this view. In the first place it implies that a part of an atom can be acting while another part is doing nothing, a state of things which it is impossible to conceive. In the next place if a compound with free affinities can exist, why should we not be able to isolate the hydrocarbon  $\begin{array}{l} | \\ CH_2 \\ | \end{array}$? This compound cannot be isolated. It is necessary to have a molecule containing at least two carbon atoms before it is possible to get a compound of the ethylene series. This makes it appear probable that the kind of unsaturation found in ethylene is dependent upon some change in the relations of the carbon atoms. The difference between the relation in ethane and in ethylene may be represented by the signs C—C and C=C. The second, or ethylene sign, suggests at once the sign used to express the carbonyl relation between carbon and oxygen. On comparing the reactions of ethylene compounds with those of carbonyl compounds, we find indeed that they have certain features in common. This is seen in their conduct under the influence of nascent hydrogen. Ethylene is converted by this reagent into the saturated compound ethane, the action being represented in this way:


$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array} + 2H = \begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}.$$

So too acetone, which may be taken as a convenient example of carbonyl compounds, takes up two atoms of hydrogen and is converted into the saturated compound, isopropyl alcohol, as represented in the equation


$$\begin{array}{ccccccccc} & & H & & O & & H & & \\ & & | & & \| & & | & & \\ H & — & C & — & C & — & C & — & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array} + 2H =$$


$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & — & C & — & C & — & C & - & H \\ & & | & & | & & | & & \\ & & H & & O & & H & & \\ & & & & | & & & & \\ & & & & H & & & & \end{array}.$$

While then it is impossible at present to say what relation the condition which we call single union bears to that which we call double union, still we cannot avoid recognising that there are at least two kinds of relations between atoms, and these two kinds may be conveniently expressed by the signs under discussion.

A similar study of acetylene, C_2H_2, and certain cyanogen derivatives, shows that, if we recognise the distinction between single and double union, we must also recognise a third kind of relation, which by analogy we should call triple union. This condition is most distinctly represented in acetylene. It carries with it the power to take up four monovalent atoms, just as the double union condition carries with it the power to take up two monovalent atoms. Acetylene becomes ethane under the influence of nascent hydrogen as expressed thus: $C_2H_2 + 4H = C_2H_6$. The same power is seen in the cyanides. Thus, methyl cyanide, which, assuming the condition of triple union between the carbon and nitrogen in the cyanogen group, is expressed thus, $CH_3—C{\equiv}N$, takes up four atoms of hydrogen, and is converted into ethylamine; thus $CH_3—C{\equiv}N + 4H = CH_3—CH_2—NH_2$; a transformation which is plainly of the same kind as that which takes place when acetylene is transformed into ethane. It should be distinctly stated that the signs used to express double union and triple union are not intended to convey the idea that the condition of single union, whatever that may be, is repeated twice or three times. They simply express relations different from that of single union, relations which we recognise by means of definite reactions. The double line certainly does not mean that the union expressed by it is twice as strong as that expressed by the single line. Indeed it is clear, from a study of compounds in which the ethylene condition exists, that the double union is less firm than the single, and the study of compounds of the acetylene order shows equally plainly that triple union is the least firm of the three.

If we should examine all the linkage formulæ of complex compounds which have been determined experimentally, we should find that, in general, the linking takes place in accordance with the laws of valency. In many cases, however, the linkages are less in number than we should be led to expect from our knowledge of the valencies of the elementary atoms. In these cases, it is generally found that the compounds have the power of forming additive compounds in which each element acts with its maximum valency.

The methods for determining constitutional formulæ thus far considered are purely chemical. They are based upon a careful study of the decompositions, syntheses, and transformations, of the compounds. The question will suggest itself, whether it is possible by a study of physical properties to throw any light upon structure. Several attempts have been made in the direction indicated. The methods will not be considered here at all in detail, as they will form the subject of other articles. The properties which have been most elaborately studied are; specific volume, molecular refraction, polarisation-phenomena, magnetic rotation, and thermal phenomena.

The specific volume, or molecular volume, of a substance is represented by a figure obtained by dividing the molecular weight of the substance by its specific gravity in the liquid form. It has been shown that the specific volume of an element in combination can sometimes be determined by studying a number of its compounds, the general principle made use of being this: the specific volume of a certain compound is determined and then that of another compound differing from the first by 1 or 2 atoms of the element; the difference between the two specific volumes is regarded as the specific volume of 1 or 2 atoms of the element by which the two compounds differ. It appears from investigations thus far carried out that the specific volume of oxygen has two values according as it is in the hydroxylic or the carbonylic condition. Assuming this to be established, it is clear that, by determining the specific gravity of a compound in liquid form, and without studying its chemical reactions, we might be able to decide whether an oxygen atom contained in it is in one or the other of the two conditions mentioned.[1]

As regards molecular refraction, it has been shown that, in general, compounds of the same composition have the same refraction-equivalent. The refraction equivalent is represented by the expression $P\left(\frac{n-1}{d}\right)$, in which P is the molecular weight of the substance, n the index of refraction, and d the relative density of the substance. A more elaborate study of this subject has shown that the molecular refraction of a substance is influenced by the presence of the condition of double or triple union. The occurrence in a compound of one double linkage causes a definite increase in the molecular refraction. So, also, the presence of carbonyl, CO, causes an increase in the molecular refraction above that found when the oxygen is present in the singly linked condition, as in hydroxyl C—O—H. If these rules can be proved to be well founded we have a method which will enable us to determine whether double linkage between carbon atoms, or between carbon and oxygen, exists in compounds under examination. The method does not, however, help us at present to understand what double linkage is. It merely puts us in a position to say that, if this condition is assumed in certain compounds, it must be assumed in certain other compounds which conduct themselves in the same way.[1]

Recently some facts have been observed in studying the magnetic rotary power of substances which may be utilised in determining constitution. It has been shown that the addition of CH_2 to a compound increases the molecular magnetic rotation by a definite quantity. So also a definite effect was shown to be produced by the introduction of methyl. Other results of the same general character were obtained. It is not improbable that a further study of the magnetic rotary power of chemical compounds may put us in possession of a method of considerable value. Up to the present the method as thus far developed has not come into general use. The method based upon a study of the magnetic rotary power, like those based upon a study of specific volumes and molecular refraction, does not give any information in regard to the various conditions which it is its object to detect. It merely attempts to tell us in which compounds certain conditions exist, without saying anything in regard to the nature of these conditions. It is, however, quite within the range of probability that continued study of all the physical properties of compounds may lead to a satisfactory hypothesis in regard to the nature of those conditions of which we now simply recognise the existence. Thus, if it is found that, whenever double linkage occurs in a compound, certain physical properties always appear, it may be possible to frame a satisfactory hypothesis in regard to the nature of the condition which we call double linkage. If then we could express this hypothesis in our formulæ, these would be, more strictly than those now in use, *constitutional formulæ.*

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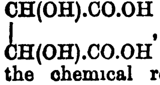
[1] The connexions between specific volume and constitution, and between refraction and constitution, are, however, not yet anything like clearly elaborated (v. PHYSICAL METHODS).—M. M. P. M.

The chemical methods and the physical methods thus far discussed have nothing directly to do with the relations which atoms bear to one another in space. The formulæ determined by means of them do not attempt to express space-relations, unless the fact that two atoms are represented as being in direct combination with each other implies that they are nearer each other than two atoms in the same molecule which are not in direct combination with each other. The formulæ simply represent connexions believed to exist between the different parts of molecules. We know nothing in regard to the forms of molecules, and the arrangement of atoms in space. Nevertheless, some ingenious speculations have been indulged in with reference to these space-relations. One which has received much attention, and which is certainly worthy of serious study, was suggested by observations of the effects produced by certain substances on polarised light. There are three varieties of tartaric acid; one of these turns the plane of polarisation of a ray of light to the right, a second turns it to the left, while the third is optically inactive. The third is formed by the union of the first and second, and is, therefore, probably to be regarded as differing from the active varieties in having a greater molecular weight.

The difference between the first and second tartaric acids cannot be expressed by means of our ordinary linkage-formulæ. Both are represented probably by the same formula,



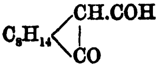
$$\begin{array}{l}CH(OH).CO.OH\\ |\\ CH(OH).CO.OH\end{array}$$

, which is in accordance with the chemical reactions, decompositions, and syntheses, of both. Nevertheless the two compounds differ. Several other cases of the same kind are known. This kind of isomerism, which shows itself in differences in the physical properties, and not in the chemical conduct, is called *physical isomerism.* To account for the particular kind of physical isomerism here referred to, Le Bel and Van't Hoff have made the suggestion that it may be due to a different arrangement in space of certain parts of the molecules. If the four affinities of a carbon atom be supposed to be exerted in the direction of the angles of a tetrahedron, the carbon atom being at the centre of the tetrahedron, there are two ways in which four different atoms or groups can be conceived to be combined with the carbon. Arranging these atoms or atomic groups in any way, the other possible arrangement is found by regarding the reflection of the first arrangement in a mirror. These two kinds of arrangement in space are possible only in those compounds in which a carbon atom is in combination with four different atoms or atomic groups. Such a carbon atom is called an *asymmetric carbon atom.* Now, it is a remarkable fact that optically active compounds always contain one or more asymmetrical carbon atoms. Some attempts have been made to express by means of formulæ the space-relations suggested in the above hypothesis (*v.* especially Wislicenus, *K. Sächsischen Ges. der Wissenschaften*, 14, 1).

It has been pointed out by Brühl that the boiling-points, densities, and indices of refraction, of isomeric compounds vary in the same way; that for isomeric compounds the constants of that one are largest which consists of an uninterrupted chain of hydrocarbon residues, and that the constants become smaller the more the structure of the molecule is branched, and deviates from one direction. The data thus far in our possession seem also to show that the shorter the molecule of isomeric compounds, *i.e.* the more they approach the spherical form, the larger is the molecular volume. The words 'shorter,' 'branched,' &c., used in these statements, have primarily, of course, reference to the appearance of the formulæ in common use, and which, as already explained, are not intended to represent the arrangement of atoms in space. But, assuming that they do in a rough way represent the shapes of the molecules, it appears that there probably exists a direct connexion between the variations in the physical constants of isomeric compounds and the shapes of their molecules. Thus, the specific gravity of compounds with long molecules would necessarily be greater than that of compounds with branched or spherical molecules, for the same reason that we can get more rods in a given space than spheres of the same weight. So also with reference to the boiling-points. The rod-shaped molecules offer the most points of contact, the spherical the fewest. The cohesion between molecules of the first kind will hence be the greatest, and the conversion of a substance made up of such molecules into vapour will require more heat, or the boiling-point will be higher, than in the case of a substance made up of molecules of the branched or spherical kind. It will thus be seen that we have faint suggestions that our linkage-formulæ have some relation to the arrangement of atoms in space, though primarily they are not intended to express facts of this order. I. R.

FORMYL. The radicle CHO, the lower homologue of acetyl. The term was at one time applied to the radicle CH now called *methenyl.* The formyl derivatives of amines are described under the amines from which they are derived.

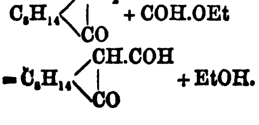
FORMYL-CAMPHOR $C_{11}H_{16}O$ *i.e.*



$$C_8H_{14}\left<\begin{array}{l}CH.COH\\ |\\ CO\end{array}\right.$$

Camphor aldehyde. [76°-78°].

Formed on treating camphor with formic ether:



$$C_8H_{14}\left<\begin{array}{l}CH_2\\ |\\ CO\end{array}\right. + COH.OEt = C_8H_{14}\left<\begin{array}{l}CH.COH\\ |\\ CO\end{array}\right. + EtOH.$$

Separated by solution in alkalis, shaking with ether, acidifying with acetic acid, shaking again with ether and evaporating (Bishop a. Claisen, *B.* 22, 533). Crystalline. Its properties are like those of the ketonic aldehydes R.CO.CHR'.COH. It is a moderately strong acid, v. sol. caustic alkalis. $FeCl_3$ gives a dark violet solution.

Salt.—A'_2Cu: bright green crystalline pp.; sl. sol. water; v. sol. organic solvents.

Anilide $C_{10}H_{11}O.CH:N.Ph$: [153°]; colourless, crystallising well.

FORMYL-TRICARBOXYLIC ACID *v.* METHANE-TRICARBOXYLIC ACID.

FORMYL CYANURAMIDE. Described under CYANIC ACID as a derivative of cyanuramide.

FORMYL-MELAMINE. Described, as a derivative of cyanuramide, under CYANIC ACID.

FORMYL-PHENYL-ACETIC ACID $HCO.CHPh.CO_2H$. *Ethyl ether* EtA'. (145°) at 16 mm. Formed by suspending dry NaOEt in ether (3 pts.), adding a mixture of formic ether and phenyl-acetic ether, and keeping the whole for several days in a closed vessel. The product is shaken with water at 0°, acidified, and extracted with ether (Wislicenus, *B.* 20, 2930). Oil. Decomposed by boiling with aqueous NaOH into formic and phenyl-acetic acids. The alcoholic solution gives a bluish-violet colouration with $FeCl_3$. Phenyl-hydrazine forms $CO\!<\!{}^{NPh.N}_{CHPh}\!>\!CH$ [196°]. Formyl-phenyl-acetic ether changes spontaneously, especially at 70°, into a crystalline isomeride [70°]; this isomeride is also split up by alkalis into formic and phenyl-acetic acids.

DI-FORMYL-PHENYLENE-DIAMINE *v.* PHENYLENE-DIAMINE.

FORMYL-PROPIONIC ACID $HCO.CHMe.CO_2H$. (161°). Formed by the action of NaOEt on a mixture of formic and propionic ethers (Wislicenus, *B.* 20, 2930). Oil. Gives an intense reddish-violet colour with $FeCl_3$.

FORMYL-UREA *v.* UREA.

FORMYL-XYLIDINE *v.* XYLIDINE.

FRAGARIANIN. Said to occur in the root of the strawberry (*Fragaria vesca*) (Phipson, *C. N.* 38, 135). V. sl. sol. water, alcohol, and ether; potash-fusion forms from it protocatechuic acid. Boiling aqueous HCl splits it up into glucose and an amorphous red substance, fragarin.

FRANCEÏNS. A group of colouring matters obtained by the action of conc. H_2SO_4 upon the haloid derivatives of benzene. From the pentachloro-benzene C_6HCl_5, the franceine has the empirical formula $C_{18}HCl_5O_3$ (Istrati, *C. R.* 106, 277; *Bl.* [2] 48, 35). All the franceïns are sol. conc. H_2SO_4, some are sol. water. Many of them dissolve in alkalis forming very soluble neutral salts. They all dissolve in alcohol forming highly-coloured dichroic solutions. They dye cotton, linen, and especially silk with shades varying from rose-colour to maroon. The depth of colour and the tinctorial power increases with the proportion of chlorine. Two franceïns $C_{18}HCl_5O_5$ are obtained by boiling pentachloro-benzene (300 g.) with Nordhausen acid (2000 c.c.) for 8 hours a day during 15 days; HCl and SO_2 are given off. At the end of 15 days the acid is decanted, a fresh quantity added, and the heating continued for another fortnight. During this process the franceïns gradually separate as a maroon-coloured substance. After washing with water, the franceïn formed in greater quantity is dissolved out in aqueous KOH, reppd. by HCl, and, when dried at 60°, exhibits a metallic green lustre. It dissolves in alcohol and in glycerine but not in water. Its alcoholic solution is red by transmitted, but yellowish-green by reflected, light, and dyes silk a rose-colour. The K salt is deep-brown with metallic lustre, and is v. sol. water forming a deep-red non-dichroic solution which gives pps. with salts of Ba, Fe, Sn, Hg, Al, Mg, Cd, Ni, &c. The second franceïn, formed at the same time in much smaller quantity from penta-chloro-benzene, is sol. warm water but almost insol. KOHAq and is less sol. alcohol than its isomeride. It dyes silk a peach colour. When tetra-chloro-benzene (200 c.c.) is boiled with conc. H_2SO_4 (1,200 c.c.) for 105 hours it is completely dissolved with evolution of water, HCl, and SO_2. No sulphonic acid is formed, but on treatment with water a reddish-brown solid is got. This solid dissolves easily in KOHAq and in alcohol; its alcoholic solution is pale brown by transmitted, and dull green, by reflected, light. According to Georgesco a. Mincou (*Bl.* [2] 50, 623), this francein is $C_{16}H_4Cl_3O_6$, and forms an insoluble silver salt $C_{16}Ag_4Cl_3O_6$.

FRANGULIN $C_{21}H_{20}O_9$? (Schwabe, *Ar. Ph.* [3] 26, 560). [230°]. A yellow crystallisable colouring matter contained in the bark of the berry-bearing alder (*Rhamnus Frangula*). It is accompanied by an amorphous yellow resin, and occurs most abundantly in the older branches, the younger branches containing more of the resin (Casselmann, *A.* 104, 77).

Preparation.—The bark is digested for three days with alcohol (90 p.c.) at 25° to 30°; the resulting tincture is concentrated by evaporation and freed from tannin &c. by ppn. with lead acetate; lead subacetate is added to the filtrate, and the pp. is suspended in alcohol and decomposed by H_2S. The boiling liquid is filtered, and on cooling deposits crystals of frangulin (Faust, *A.* 165, 229; *Z.* [2] 5, 17; Liebermann a. Waldstein, *B.* 9, 1775).

Properties.—Lemon-yellow crystalline mass with dull silky lustre. Insol. water; soluble in 160 pts. of warm dilute (80 p.c.) alcohol, nearly insol. cold alcohol, sl. sol. ether, sol. hot fixed oils, benzene, and oil of turpentine. May be partially sublimed as minute golden needles (C.). In aqueous alkalis it forms a deep cherry-red solution from which it is reppd. by acids but not by metallic salts. Conc. H_2SO_4 forms a dark-red solution which becomes brown on heating; it is reppd. by water. Boiling conc. HNO_3 dissolves it without decomposition (C.). Fuming HNO_3 forms oxalic acid and so-called 'nitro-frangulic acid' $C_{20}H_{11}N_5O_{18}$? (Hesse, *A.* 117, 349) which crystallises in orange-red needles (from alcohol). Frangulin is split up by boiling dilute HCl into glucose and emodin, a tri-oxy-methyl-anthraquinone (Schwabe).

FRAXIN $C_{16}H_{18}O_{10}\frac{1}{2}aq$. *Paviin.* A substance occurring in the bark of the common ash (*Fraxinus excelsior*), and also, together with æsculin, in the bark of the horse-chestnut (*Æsculus Hippocastanum*), and in various species of *Pavia* (Salm-Horstmar, *P.* 97, 327, 637; 100, 607; Rochleder, *P.* 107, 331; *J. pr.* 90, 433; Stokes, *C. J.* 9, 17; Keller, *Rep. Pharm.* 44, 438; Rochleder a. Schwarz, *A.* 87, 186; Stenhouse, *P. M.* [4] 7, 501).

Preparation.—1. A decoction of ash-bark (taken at the flowering-time) is ppd. by lead acetate; the filtrate is ppd. by lead subacetate, and the pp. suspended in water and decomposed by H_2S (Salm-Horstmar).—2. The aqueous decoction of horse-chestnut bark is mixed when cold with such a quantity of $FeCl_3$ that on adding ammonia the pp. immediately separates; one-fourth of the ammoniacal filtrate is ppd. by lead acetate, the pp. is redissolved in HOAc, the rest of the filtrate is then acidified by acetic acid, the two portions mixed together, and, after again adding ammonia, the resulting pp. dissolved in acetic acid, freed from lead by H_2S, and left to crystallise.

Properties.—Tufts of colourless needles; it has a slightly bitter taste. Sl. sol. cold, v. sol. hot, water; sl. sol. cold, m. sol. hot alcohol; insol. ether (Salm-Horstmar). Stokes (*C. J.* 12, 17) found it more soluble in ether than æsculin. It gives off its water of crystallisation at 110° to 150°, and melts at a higher temperature (320° according to Salm-Horstmar). The concentrated aqueous solution is yellow, and has an acid reaction; when largely diluted it exhibits strong bluish-green fluorescence; this fluorescence is increased by the presence of a trace of alkali, but is destroyed by acids. The alcoholic solution is likewise fluorescent. $FeCl_3$ colours the aqueous solution green, and then yields a lemon-yellow pp. Lead acetate also gives a yellow pp. in its ammoniacal solution. Boiling dilute H_2SO_4 splits fraxin up into glucose and fraxetin.

Fraxetin $C_{10}H_8O_5$. S. (cold) ·1; (hot) ·33. Formed as above, and also by the action of HCl on a lemon-yellow crystalline compound $C_{22}H_{28}O_{15}$, also occurring in horse-chestnut bark (Rochleder, *C. C.* 1864, 415). Needles (from the dilute H_2SO_4 in which it is formed), or tables (from alcohol). Has a slightly astringent taste. V. sl. sol. water, sl. sol. alcohol and ether. Melts at the melting-point of tin, without turning brown. Conc. H_2SO_4 forms a bright-yellow solution, whence after dilution and addition of NH_3 it separates in crystals. HClAq dissolves it. Conc. HNO_3 is coloured by it dark-violet, changing to red and yellow. The aqueous solution is coloured yellow by NH_3. $FeCl_3$ colours its aqueous solution greenish-blue. Acid ammonium sulphite dissolves fraxetin, and on adding NH_3 the liquid becomes yellow, but does not turn red or blue on shaking with air (difference from æsculetin).

FUCUS ALDEHYDE $C_5H_4O_2$. *Fucusol. (β)-Pyromucic aldehyde.* (172°). S.G. $^{\underline{15\cdot5}}$ 1·150. S. 7 at 13°. A volatile oil, isomeric or possibly identical with furfurol, obtained by distilling sea-weeds (*Fucus nodosus, F. vesiculosus, F. serratus*, &c.) with dilute sulphuric acid (Stenhouse, *P. M.* [3] 18, 122; 37, 226; *A.* 35, 301; 74, 278). It is washed free from accompanying acetone, distilled with steam, and dried over $CaCl_2$. Colourless oil; turns brown on keeping exposed to air. H_2SO_4 colours it yellowish-brown; HClAq turns it green; when impure the colour in both cases is purple-red. KOHAq colours it yellow, the colour afterwards changing to dark-red. Fucusol turns the skin deep-yellow, the spots being turned rose-red by aniline (as with furfurol). When boiled with water and moist Ag_2O the silver salt of (β)-pyromucic acid is formed $C_5H_3AgO_3$; (β)-pyromucic acid prepared from this salt crystallises in small rhomboidal plates [130°], whereas ordinary pyromucic acid forms flat needles [133°] (Stenhouse, *Pr.* 20, 80). Ammonium sulphide converts fucusol into thiofucusol C_5H_4SO, which resembles its isomeride thiofurfurol. Moss (*Sphagnum*) and various species of lichen (*Cetraria islandica, Usnea*, and *Ramalina*) when distilled with dilute H_2SO_4 yield an oil apparently identical with fucusol.

Fucusamide $C_{15}H_{12}N_2O_3$. S. ·04 at 8°. This isomeride of furfuramide is obtained by the action of ammonia on fucusol. It crystallises from hot alcohol in groups of long needles. Its reactions are similar to those of furfuramide.

Fucusine $C_{15}H_{12}N_2O_3$. When fucusamide is boiled for twenty minutes with moderately concentrated aqueous KOH it melts, and is converted into an oil which solidifies on cooling to a yellowish resin. From this resin HNO_3 extracts the base, and, on cooling, the nitrate crystallises out. If a slight excess of NH_3 be added to an aqueous solution of the nitrate fucusine slowly separates in stellate groups of small laminæ.

Salts.—$B'HNO_3$: stellate groups of long prisms (from water), or large trimetric prisms (from alcohol). Decomposes at 100°. — $B'_2H_2PtCl_6$: four-sided prisms (the corresponding salt of furfurine forms needles).—$B'H_2C_2O_4$: small silky needles; m. sol. cold water.

FULMINATES. Described under CYANIC ACID.

FULMINURIC ACID. Described under CYANIC ACID.

FUMARAMIC ACID *v. Amide* of FUMARIC ACID.

FUMARANILIC ACID *v. Anilide* of FUMARIC ACID.

FUMARIC ACID $C_4H_4O_4$ *i.e.* $CO_2H.CH{:}CH.CO_2H$. *Allo-maleic acid.* Mol. w. 116. S. ·67 at 16·5° (Carius, *A.* 142, 153); (cold 70 p.c. alcohol) ·48. H.C. 318,176 (Louguinine, *C. R.* 106, 1290). *Heat of solution* −5901 (Gal a. Werner, *Bl.* [2] 47, 159). *Heat of neutralisation* (by NaOH) 26599 (G. a. W.).

Occurrence.—In various plants and fungi: fumitory (*Fumaria officinalis*), *Corydalis bulbosa, Glaucium flavum*, Iceland moss (*Lichen islandicus*), *Boletus pseudo-ignarius*, and *Agaricus piperatus* (Winkler, *Rep. Pharm.* 39, 48, 368; 48, 39, 363; *A.* 4, 230; Wicke, *A.* 87, 225; Probst, *A.* 31, 248; Pfaff, *Schw. J.* 47, 476; Dessaignes, *J. Ph.* [3] 32, 48; *A.* 89, 120; Bolley, *A.* 86, 44; Schödler, *A.* 17, 148; Trommsdorff, *N. Tr.* 25, 2, 153).

Formation.—1. Together with maleïc acid by the dehydration of malic acid by heat (Lassaigne [1819], *A. Ch.* [2] 11, 93; Pelouze, *A. Ch.* [2] 56, 429; *A.* 11, 265).—2. From maleic acid by heating with aqueous HI, HBr, or HCl (Dessaignes, *J.* 1856, 463; Kekulé, *A.* 130, 21; *Suppl.* 2, 85).—3. By treating calcium malate with PCl_5, and decomposing the resulting chloride with water (Perkin a. Duppa *A* 112, 24).—4. By fusing sulpho-succinic acid with potash

(Messel, *A.* 157, 20).—5. By heating bromo-succinic acid.—6. By the action of aqueous KI and copper upon di-bromo-succinic acid and its isomeride (Swarts, *Z.* 1868, 259). Also from di-bromo-succinic acid and thio-urea (Nencki a. Sieber, *J. pr.* [2] 25, 72).—7. From di-bromo-succinic ether by treatment with finely divided silver and saponification of the product (Gorodetzky a. Hell, *B.* 21, 1802).—8. By heating succinimide with bromine at 130° in sealed tubes (Kisielinski, *Sitz. W.* 74, 561).—9. By boiling silver malonate with di-chloro-acetic acid and a little water (Komnenos, *A.* 218, 169).—10. By treating asparagin or aspartic acid with MeI and KOH (Körner a. Menozzi, *G.* 13, 352).—11. From (δ)-bromo-pyromucic acid, bromine, and water (Hill a. Sanger, *A.* 232, 53; *cf.* Limpricht, *A.* 165, 289).—12. By treating β-di-chloro-propionic ether with KCy, and decomposing the product by KOH (Werigo a. Tanatar, *A.* 174, 368).—13. By boiling chloro-ethane-tricarboxylic ether (prepared by the action of Cl on ethane tricarboxylic ether $(CO_2H)CH_2.CH(CO_2H)_2$ with HCl (Bischoff, *B.* 13, 2162).—14. According to Mühlhäuser (*A.* 101, 171) fumaric acid is among the products of the action of aqua regia on proteïd compounds.—15. By heating ethylene tetra-carboxylic acid (Conrad a. Guthzeit, *B.* 16, 2632).

Preparation.—Malic acid is heated at 150°, and finally to 180°, in a current of air as long as water and maleïc acid distil out. The residue is washed with a little cold water and dried at 100°. 250 g. malic acid treated in this way give 160 g. fumaric acid (Purdie, *C. J.* 39, 346; *cf.* Baeyer, *B.* 18, 676).

Properties.—Small prisms, needles, or plates. Sublimes at 200°, and when strongly heated it gives some maleïc anhydride. It burns with a pale flame. The initial rate of etherification of fumaric acid (32·7) is less than that of maleïc acid (51·5), but ultimately the same proportion of each (72·6 p.c.) is etherified by isobutyl alcohol (Menschutkin, *B.* 14, 2630).

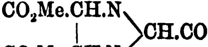
Reactions.—1. *Reduced* to succinic acid by adding sodium-amalgam to its aqueous solution, or by heating with HIAq.—2. Heated with HBrAq at 120° it is slowly transformed into bromo-succinic acid.—3. It combines very slowly with *bromine* in the cold, but when heated with bromine and water at 100° di-bromo-succinic acid is formed in a few minutes (Kekulé, *A. Suppl.* 1, 129; Petrie, *A.* 195, 56).—4. *Zinc* dissolves in aqueous fumaric acid, forming zinc-fumarate, and giving off hydrogen (Kekulé, *A. Suppl.* 2, 108). When zinc and fumaric acid are placed together in cold water hydrogen is not evolved, but zinc fumarate is formed, while succinic acid remains in solution (Von Victor, *Z.* [2] 4, 454). When fumaric acid is gently heated with zinc and excess of potash-solution it is reduced to succinic acid (K.).—5. Fumaric acid is not *oxidised* by boiling HNO_3, by water and PbO_2, or by $K_2Cr_2O_7$. Aqueous $KMnO_4$ oxidises it to racemic acid.—6. *Electrolysis* of an aqueous solution of sodium fumarate gives acetylene, CO_2, and hydrogen (Kekulé, *A.* 131, 85).—7. *Chlorine* forms di-chloro-succinic and tri-chloro-acetic acids (Pétrieff, *Bl.* [2] 41, 309).—8. *Hypochlorous acid* forms a compound $(CO_2H.CHCl.CH(OH).CO_2H)$, which yields inactive malic acid when reduced by sodium-amalgam (P.).—9. Aqueous NaOH at 100° slowly forms inactive malic acid.—10. *Water* in large quantity at 150° also forms inactive malic acid (Jungfleisch, *B.* 12, 370; Pictet, *B.* 14, 2648).—11. Boiling aqueous K_2SO_3 forms potassium sulpho-succinate.—12. *Acetyl chloride*, in presence of HOAc at 100°, dissolves fumaric acid in twenty-four hours, the product being maleïc anhydride (Perkin, *C. J.* 39, 560; 41, 268), while, according to Anschütz (*B.* 10, 1881; 14, 2792), pure AcCl has no action on fumaric acid. By heating fumaric acid with pure AcCl at 140° Perkin (*B.* 15, 1073) obtained maleïc anhydride and a little chloro-succinic anhydride; the latter being probably an intermediate body in the formation of maleïc anhydride (Anschütz a. Bennert, *B.* 15, 640).—13. *Fumaric chloride* alone, or dissolved in benzene, reacts with silver fumarate, forming maleïc anhydride. Fumaric chloride, dissolved in light petroleum, is converted by Na_2CO_3 into maleïc anhydride. It is evident, therefore, that there is but one anhydride for the two isomeric acids, fumaric and maleïc.—14. A dilute aqueous solution containing fumaric acid and *aniline* in proportion to form the acid aniline salt gives, on heating, no anilide (difference from maleïc acid) (Michael, *Am.* 9, 180).—15. Excess of alcoholic *ammonia* at 150° for twenty hours forms inactive aspartic acid (Engel, *C. R.* 104, 1805).

Salts.—None of the fumarates dissolve in alcohol. Solutions of the alkaline fumarates are not ppd. by salts of Zn, Al, or Cr.—$(NH_4)_2A''$: v. sol. water, converted into the acid salt by evaporation.—$(NH_4)HA''$: monoclinic prisms (Delffs, *P.* 80, 435; Pasteur, *A. Ch.* [3] 31, 91).—$K_2A''2aq$: large transparent trimetric tables and four-sided prisms or radiating groups of laminæ. V. sol. water; from a concentrated solution acetic acid throws down the acid salt.—KHA'': tufts of needles, sl. sol. cold, v. sol. hot, water (Carius, *B.* 4, 929; *A.* 142, 153).—$K_2H_4A''_3$: acicular prisms. S. 2·66 at 19·5°.—$Na_2A''aq$: crystalline powder; ppd. by adding alcohol to its aqueous solution.—$Na_2A''3aq$: needles and prisms. V. sol. cold water.—Ag_2A'': fine white powder, thrown down by adding $AgNO_3$ to a solution of (even 1 pt. in 200,000 of) fumaric acid. Deflagrates when heated. Insol. water, sol. HNO_3Aq and NH_3Aq.—$Ag_2A''aq$ (Carius): sol. hot water.—BaA''. Obtained by dissolving fumaric acid in a hot solution of barium acetate (fumaric acid does not ppt. baryta water). Crystalline grains.—$BaA''1\frac{1}{2}aq$. From K_2A'' and $BaCl_2$. Small efflorescent prisms. S. (of BaA'') ·966 at 17°.—$BaA''3aq$: small white prisms. Converted by boiling with water into insoluble grains of BaA'' (Anschütz, *B.* 12, 2282).—$SrA''3aq$: from fumaric acid and SrO_2Ac_2. Crystalline powder, sl. sol. water.—$CaA''3aq$. Occurs in fumitory. From K_2A'' and CaO_2Ac_2. Shining scales, sl. sol. water, permanent in the air. Gives calcium succinate when exposed in contact with fermenting cheese to the air.—$CaA''1\frac{1}{2}aq$ (dried over H_2SO_4).—$MgA''4aq$: white powder.—Hg_2A'': white crystalline pp. (Rieckher, *A.* 49, 31).—$PbA''2aq$. Formed by heating lead malate to 200° (R.). Also from K_2A'' and aqueous PbO_2Ac_2 acidulated with HOAc. Tufts of shining needles. Nearly insol. cold, sol. hot, water; insol. HOAc; sol. HNO_3Aq.—$PbA''3aq$ (Pelouze).—$A''(PbOH)_2$

(at 100°). Ppd. by adding ammonic fumarate to boiling aqueous lead subacetate (Otto, *A.* 127, 178).—$(PbA'')_2PbO\,x$aq (R.).—$PbA''(PbO)_2\,x$aq (R.).—CuA″ 3aq. From CuO_2Ac_2 and fumaric acid. Bluish-green crystalline powder; sl. sol. water, v. sol. HNO_3Aq.—A″FeOH. Pale brownish-red pp. formed by adding $FeCl_3$ to ammonium fumarate: insol. excess of ammonium fumarate (difference from succinate); insol. NH_3Aq, sol. mineral acids.—NiA″ 4aq: pale-green powder, sol. water and ammonia solution.—CoA″ 3aq. Obtained by adding alcohol to a concentrated solution of fumaric acid in aqueous CoO_2Ac_2. Rose-coloured powder, v. sol. water and NH_3Aq. —MnA″ 3aq. From fumaric acid and MnO_2Ac_2. White powder, sl. sol. water.—ZnA″ 3aq: large prisms (from hot solutions), v. sol. water.—ZnA″ 4aq: efflorescent crystals (by spontaneous evaporation).

Methyl ether Me_2A''. [103°]. (192° i. V.).

Formation.—1. By the action of HCl or H_2SO_4 on fumaric acid in MeOH (Anschütz, *B.* 12, 2282; Ossipoff, *J. R.* 11, 288).—2. By the action of iodine on methyl maleate.—3. From methyl bromo-succinate by treatment with KCy in ether, or by subliming the same ether with NaOAc and $CaCO_3$ (Volhard, *A.* 242, 160).—4. By the action of NaOMe on a solution of fumaric ether in MeOH (Purdie, *C. J.* 51, 627).—5. By boiling methyl diazo-succinate with water or MeOH (Curtius a. Koch, *B.* 18, 1296).

Properties.—Triclinic prisms (Bodewig, *Z. K.* 5, 563). Sl. sol. water, alcohol, ether, and CS_2 in the cold. Combines with bromine forming methyl di-bromo-succinate [62°]. With an equivalent quantity of diazo-acetic methyl ether it forms  $\left.\begin{array}{l}CO_2Me.CH.N\\ \quad\quad|\\ CO_2Me.CH.N\end{array}\right\rangle CH.CO_2Me$, an oil, whence the corresponding acid [220°] may be obtained (Buchner, *B.* 21, 2637).

Mono-ethyl ether EtHA″. Formed by heating fumaric acid (2 pts.) with alcohol (3 pts.) at 120° (Laubenheimer, *A.* 164, 297). Plates, sl. sol. water, v. e. sol. alcohol and ether.—AgEtA″. S. ·3 at 12°. Crystalline pp.

Di-ethyl ether Et_2A''. (215° uncor.) (P.); (218° i. V.) (A.). S.G. $^{\underline{17\cdot5}}$ 1·052 (A.); $^{\underline{11}}$ 1·106 (H.). V.D. 85·5 (calc. 86). M.M. 10·119 (Perkin, *C. J. Proc.* 3, 98).

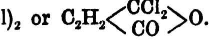
Formation.—1. By treating an alcoholic solution of fumaric or malic acid with HCl (Hagen, *A.* 38, 274). Some chloro-succinic ether is formed at the same time.—2. By boiling fumaric acid (149 g.) with alcohol (450 g.) and H_2SO_4 (15 g.), ppg. by water, drying over $CaCl_2$, and distilling. The yield is good (123 g.) (Purdie, *C. J.* 39, 346).—3. From malic ether and PCl_5 (Henry, *A.* 156, 177).—4. From EtI and silver fumarate (Anschutz, *B.* 11, 1644; 12, 2282).—5. By the action of finely divided silver on di-bromo-succinic ether (Gorodetzky a. Hell, *B.* 21, 1802).

Reactions.—1. Combines with bromine forming di-bromo-succinic ether [58°] (Ossipoff).—2. Combines with NaOEt (in alcoholic solution) forming $CO_2Et.CHNa.CH(OEt).CO_2Et$. If the product is boiled with aqueous NaOH, neutralised with acetic acid and treated with $Pb(OAc)_2$, lead fumarate is ppd. The filtrate is acidulated with HNO_3, neutralised with NH_3, and treated with $Pb(NO_3)_2$, when a lead salt is ppd., whence H_2S liberates a crystalline acid $C_6H_{10}O_5$ or $CO_2H.CH_2.CH(OEt)CO_2H$, [86°] (*v.* MALIC ACID) (Purdie, *C. J.* 39, 347). Sodium fumarate differs from ethyl fumarate in not combining with NaOEt.—3. NaOMe (in methyl alcoholic solution) reacts in a similar way forming first methyl fumarate and then $CO_2Me.CH_2.CH(OMe).CO_2Me$ or its sodium derivative (Purdie, *C. J.* 47, 855). 4. By heating with alcoholic NH_3 in sealed tubes there is formed aspartic ether (152° at 25 mm.) together with a compound $C_4H_6N_2O_2$ [c. 250°], possibly an imide of aspartic acid (Körner a. Menozzi, *G.* 17, 226).

Iso-butyl ether $(PrCH_2)_2A''$. (170°) at 160 mm. From silver fumarate and isobutyl iodide (Purdie, *C. J.* 39, 353). Not obtained quite pure. Combines with sodic isobutylate in presence of isobutyl alcohol forming a product whence, on saponification, the isobutyl derivative of malic acid (*q. v.*) is got.

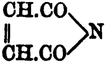
Phenyl ether $(C_6H_5)_2A''$. [162°]. From fumaryl chloride and phenol. White needles, sl. sol. alcohol. On heating it evolves CO_2, yielding phenyl cinnamate and finally stilbene $C_6H_5.C_2H_2.C_6H_5$ (Anschütz a. Wirtz, *B.* 18, 1948; *C. J.* 47, 898).

p-Tolyl ether $(C_7H_7)_2A''$: [162°]; v. sl. sol. alcohol. On heating it gives *s*-di-tolyl-ethylene $C_7H_7.C_2H_2.C_7H_7$ [179°], and a substance crystallising in scales [79°] (A. a. W.).

Chloride $C_2H_2(COCl)_2$ or  $C_2H_2\left\langle\begin{array}{c}CCl_2\\ CO\end{array}\right\rangle O$. *Maleyl chloride.* (160°). From malic acid and PCl_5 (Perkin a. Duppa, *A.* 112, 26). Formed also by the action of PCl_5 on fumaric acid or maleïc anhydride (Kekulé, *A. Suppl.* 2, 86; Perkin, *B.* 14, 2548). Bromine at 150° combines with it, forming di-bromo-succinyl chloride.

Mono-amide $CO_2H.CH:CH.CONH_2$. *Fumaramic acid. Anhydro-aspartic acid.* [217°]. Prepared by the action of methyl iodide and caustic potash on asparagine $C_4H_8N_2O_3 + 4MeI = C_4H_5O_3N + NMe_4I + 3HI$ (Griess, *B.* 12, 2117; Michael a. Wing, *Am.* 6, 420). Leaflets, sol. hot water and hot alcohol, almost insol. ether. Decomposed by alkalis or acids into NH_3 and fumaric acid. Combines with bromine (1 mol.). Salts.—BaA'_2 6aq: plates, sl. sol. water.—AgA′: small needles or leaflets, sol. hot water. *Methyl ether* A′Me: [162°]; small colourless tables; sublimable; sl. sol. cold water, v. sol. alcohol. Formed by the action of cold, slightly acidulated, water on methyl diazo-succinamate $CO_2Me.CH_2.CN_2.CO_2Me$ (Curtius a. Koch, *B.* 19, 2461).

Amide $C_4H_6N_2O_2$ *i.e.* $CONH_2.CH:CH.CONH_2$. [232°]. From fumaric ether and cold aqueous ammonia (Hagen, *A.* 38, 275). Small white needles (Curtius a. Koch, *B.* 18, 1296). Insol. cold, sol. hot water, insol. alcohol. When heated for some time with water it is converted into ammonium fumarate. HgO is converted by boiling with its aqueous solution into a white powder $C_4H_6N_2O_2HgO$ (Dessaignes, *A.* 82, 233).

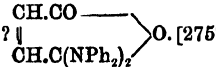
Imide? $C_4NH_3O_2$ *i.e.*  $\left.\begin{array}{l}CH.CO\\ \|\\ CH.CO\end{array}\right\rangle NH$? Formed by heating acid ammonium malate at 160° to 200° (Dessaignes, *C. R.* 30, 324; Wolff, *A.* 75, 293). White powder; sol. hot conc. HClAq and reppd. by water. By heating for 6 hours with HClAq it is converted into aspartic acid. Acid ammonium maleate and fumarate yield on heating to 180° substances resembling this so-called 'fumarimide' (Pasteur, *A. Ch.* [3] 34, 30).

Di-ethyl-amide $C_2H_2(CO.NHEt)_2$. [183°]. White scales; may be sublimed (Wallach a. Kamenski, *B.* 14, 170).

Mono-anilide $CO_2H.CH{:}CH.CO.NHPh$. *Fumaranilic acid.* [187°]. From the phenyl-imide of maleïc acid by treatment with baryta-water at 35° (Anschütz a. Wirtz, *Am.* 9, 240; *A.* 239, 137). Formed also when maleïc anhydride, dissolved in ether, is mixed with aniline (Anschütz, *B.* 20, 3214). Prisms, sl. sol. water. Converted by alcoholic KOH into potassium fumarate.

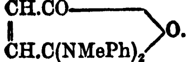
Di-anilide $C_2H_2(CO.NHPh)_2$. Formed by the action of aniline upon fumaryl chloride, both being in ethereal solution (Anschütz a. Wirtz, *Am.* 9, 236). Minute white needles, browning at 275°, v. sl. sol. ether, sl. sol. alcohol and glacial acetic acid. Heated at 100° with alcoholic KOH it gives aniline and fumaric acid. Takes up Br (1 mol.), forming a white powder; not melted at 100°.

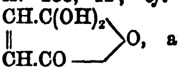
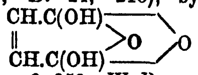
Di-phenyl-amic acid $CONPh_2.CH{:}CH.CO_2H$. *Di-phenyl-fumaramic acid.* [120°]. Formed by heating fumaric or malic acid with di-phenyl-amine at 210°; extracting the product with ether, shaking the ethereal solution with dilute NH_3, and ppg. by HCl (Piutti, *G.* 16, 22, 133). Small needles; sol. alcohol and conc. H_2SO_4, the solution giving with nitric acid the blue reaction of diphenylamine. Decomposed by KOH into fumaric acid and diphenylamine. Unites with Br forming a crystalline product. Its alkaline solution gives a light green pp. with cupric salts.

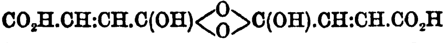
Di-phenyl-imide?  [275°].

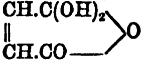
Formed by heating fumaric or maleïc acid with di-phenyl-amine at 225° as long as water is given off (Piutti). Glistening needles, sol. HOAc. With conc. HNO_3 it yields a nitro- compound giving a violet colouration with alcoholic KOH.

Phenyl-methyl-amic acid $CONMePh.CH{:}CH.CO_2H$. [128°]. Formed by heating malic acid (1 mol.) with methyl-aniline (not more than 2 mols.) at 150° (Piutti, *G.* 16, 24). It is also one of the products of the action of NH_3 on phthalyl-aspartic acid. Long tabular prisms (containing aq); melting at 100° when hydrated, and at 128° when anhydrous. Insol. water, sol. alcohol and ether. Its alkaline salts are very soluble; its silver salt forms small glistening prisms. Its di-bromo- derivative [178°] forms glistening prisms, partly decomposed on recrystallisation.

Phenyl-methyl-imide? $C_{18}H_{18}N_2O_2$ *i.e.*  [187°]. Formed by heating malic acid with methyl-aniline at 200°. It is also one of the products of the action of phenyl-methyl-amine on phthalyl-aspartic acid at 240°. Glistening prisms, sol. hot alcohol and chloroform. When heated with conc. HClAq at 180° it yields fumaric acid and methyl-aniline. Br in chloroform forms a di-bromo- derivative $C_{18}H_{16}Br_2N_2O_2$ [c. 207°].

Constitution.—Inasmuch as both fumaric and maleïc acids are dibasic acids formed from malic acid by elimination of water, and capable of reduction to succinic acid, they ought both to be represented by the formula $C_2H_2(CO_2H)_2$. One or both of them would then be $CO_2H.CH{:}CH.CO_2H$. The usual interpretation given to structural formulæ will not in this case account for the isomerism, and it will be necessary, if we assign the formula $CO_2H.CH{:}CH.CO_2H$ to both maleïc and fumaric acid, to consider that the difference in structural formula is one that cannot be represented on a plane surface but only in space. Various attempts have been made to express a difference in structure upon paper. Thus while the formula $CO_2H.CH{:}CH.CO_2H$ has commonly been assigned to fumaric acid, maleïc acid has been represented by $CO_2H.CH_2.C.CO_2H$ (Fittig, *A.* 188, 42; *cf.* Hübner, *B.* 14, 210), by  and by  (Anschütz, *A.* 239, 161; *Am.* 9, 253; W. Roser, *A.* 240, 133). Erlenmeyer, on the contrary, suggests that maleïc acid is $CO_2H.CH{:}CH.CO_2H$, while fumaric acid may have the double formula



(*B.* 19, 1936), although Raoult's method of determining molecular weights indicates that this is not the case (Paternò, *B.* 21, 2158). Maleïc acid is much more prone to react with other bodies than fumaric acid, and this would be represented by the formula $CO_2H.CH_2.C.CO_2H$, containing a divalent carbon atom, and perhaps also by the anhydride formula  of Anschütz. Thus maleic acid combines at once with HBr and with bromine, whereas fumaric acid requires to be heated (in the case of Br the products are different). Again acid aniline maleate readily splits off water when its aqueous solution is left to stand for a few days, or when it is boiled, a crystalline pp. of the acid anilide $CO_2H.C_2H_2.CONHPh$ being formed; under these conditions the acid aniline fumarate is quite stable (Michael, *B.* 19, 1372). The chemical differences here noted between fumaric and maleïc acids hold good also between citraconic and mesaconic acids, and between (α)-coumaric and (β)-coumaric acids. There is also but one anhydride to each of these pairs of acids. The fact that fumaric acid, on oxidation by $KMnO_4$, gives racemic acid, while maleic acid gives inactive tartaric acid, has been explained by Le Bel by the aid of formulæ represented in three dimensions (*v.* also Lossen, *B.* 20, 3310; Anschütz, *B.* 21, 518). According to Knops (*A.* 248, 175) the molecular refraction of fumaric and maleïc acids and their ethers indicates that both these acids contain the group C:C. The term 'allo-isomerism' has been applied to such cases of isomerism as that here described: fumaric acid may be called allo-maleïc acid.

References.—MALEÏC ACID, BROMO-FUMARIC ACID, and CHLORO-FUMARIC ACID.

FUMARINE. An alkaloid contained in fumitory (*Fumaria officinalis*) (Peschier; Hannon, *J. Chim. Méd.* [3] 8, 705; Preuss, *Z.* [2] 2, 414; *Bl.* [2] 7, 453). The plant gathered in full flower may contain 5 p.c. of fumarine. The plant is extracted by dilute acetic acid at 100°, the extract evaporated, the syrupy residue dissolved in alcohol, and decolourised by animal charcoal. Fumarine acetate crystallises from the alcoholic solution in slender needles. Aqueous KOH and Na_2CO_3 separate fumarine from its salts as a curdy pp. It crystallises in six-sided irregular monoclinic prisms, sl. sol. water, insol. ether, sol. alcohol, chloroform, benzene, and CS_2. Its solution has a bitter taste and alkaline reaction. Conc. HNO_3 does not colour it. Conc. H_2SO_4 forms a dark-violet liquid. Its hydrochloride and sulphate crystallise in prisms, sl. sol. water; its platinochloride and aurochloride crystallise in octahedra.

FUMARYL CHLORIDE *v. Chloride* of Fumaric acid.

FURFURACROLEÏN *v.* Furfuryl-acrylic aldehyde.

FURFURACRYLIC ACID *v.* Furfuryl-acrylic acid.

FURFURAL *v.* Furfuraldehyde.

FURFURAL-*compounds* *v.* Furfuryl methylene *compounds.*

FURFURAL-ACETOACETIC ETHER. Described under Aceto-acetic acid.

FURFURAL-ACETONE *v.* Furfuryl-vinyl methyl ketone.

FURFURAL-BENZYLIDENE-ACETONE *v.* Furfuryl-vinyl styryl ketone.

FURFURAL-CARBAMIC ETHER *v.* Furfuryl-methylene-dicarbamic ether.

FURFURALCOHOL *v.* Furfuryl-carbinol.

FURFURALDEHYDE $C_5H_4O_2$ *i.e.* $C_4H_3O.CHO$. *Pyromucic aldehyde. Furfurol. Furfural. Furfurane-carboxylic aldehyde* (*Furfur* = bran). Mol. w. 96. (162°) (Brühl, *A.* 235, 7). V.D. 3·34 (calc. 3·32). S.G. $\frac{20}{4}$ 1·1594 (B.). S. 9 at 13° (Stenhouse); 8·3 at 15·6° (Fownes). μ_D 1·5261 (B.). S.V. 95·53 (R. Schiff, *A.* 220, 103); 103 (Ramsay). H.F.p. 5985 (Ramsay, *C. J.* 35, 703). *Dispersion value*: Brühl, *A.* 236, 259.

Occurrence.—Has been observed in brandy (Morin, *C. R.* 105, 1019), and is a constant impurity in isoamyl alcohol prepared from fusel oil (Udránsky, *H.* 13, 248).

Formation.—1. A general product of the destructive distillation of the carbohydrates or of substances containing them, such as wood. Formed also in the torrefaction of coffee and cocoa and occurs in tobacco smoke (Völckel, *A.* 85, 65; Hill, *Am.* 3, 36; H. Schiff, *G.* 17, 355; Gaus, Stone, a. Tollens, *B.* 21, 2148; V. Meyer, *B.* 11, 1870; Förster, *B.* 15, 322; Jorisson, *B.* 15, 574).—2. By distilling the following substances with dilute sulphuric acid: bran, starch, oatmeal, sugar, madder, sawdust, linseed cake, cocoa-nut shells, mahogany, and even, according to Udránsky (*H.* 12, 377), of proteids (Doebereiner [1831] *Schw. J.* 63, 368; *A.* 3, 141; Stenhouse, *P. M.* [3] 18, 122; 37, 226; *A.* 35, 301; 74, 278; 156, 197; Fownes, *Tr.* 1845, 253; *A.* 54, 52; *Ph.* 8, 113; Cahours, *A. Ch.* [3] 24, 277; Emmet, *Am. S.* 32, 140; Gudkoff, *Z.* 1870, 362; Guyard, *Bl.* [2] 41, 289).—3. By distilling sugar with MnO_2 and dilute sulphuric acid.—4. By heating bran with a very strong solution of $ZnCl_2$ (Von Babo, *A.* 85, 100).—5. By heating wood shavings with water for four hours at 200° (Greville Williams, *C. N.* 26, 231, 293; H. Müller, *C. N.* 26, 247).—6. Formed in small quantity by boiling sugar with water; this accounts for its occurrence in brandy (Förster, *B.* 15, 230, 322). 7. One of the products obtained by heating (*a*)-acrosone to 140° (E. Fischer a. Tafel, *B.* 22, 99). Obtained also by heating a dilute aqueous solution of glucosone in a sealed tube at 140° (E. Fischer, *B.* 22, 93).—8. By heating a 5 p.c. aqueous solution of mannite in a closed tube for 4 hours at 140° (E. Fischer a. Hirschberger, *B.* 22, 369).

Preparation.—1. By distilling sugar (1 pt.) with MnO_2 (3 pts.), H_2SO_4 (3 pts.), and water (5 pts.); the distillate is neutralised by Na_2CO_3, redistilled, and saturated with $CaCl_2$ (Doebereiner).—2. H_2SO_4 (100 pts.), water (300 pts.), and bran (100 pts.) are distilled together. The product is neutralised by Na_2CO_3, redistilled, saturated with NaCl and re-distilled (Schwanert, *A.* 116, 257). The yield is small (less than 3 pts.). The crude furfuraldehyde is treated with dilute H_2SO_4 and a little $K_2Cr_2O_7$ to remove 'metafurfural,' dried over $CaCl_2$, and rectified.—3. An abundant source of furfuraldehyde is in the preparation of 'garancin' by boiling madder with dilute sulphuric acid.

Impurity.—Crude furfuraldehyde is liable to contain a readily oxidisable oil of higher boiling-point, which is for the most part resinified during the distillations. When this 'metafurfurol' is present the furfuraldehyde gives a purple colour when mixed with a few drops of conc. H_2SO_4, of HClAq, or of HNO_3; in this case also the aldehyde, after boiling with aqueous KOH, turns red on acidification.

Properties.—Colourless oil which, except when quite pure, slowly turns brown when exposed to light. Its odour resembles that of a mixture of the oils of cinnamon and of bitter almonds. It burns with a smoky flame. Furfuraldehyde when present in a liquid imparts a rose-red colour to paper saturated with aniline acetate (Guyard, *Bl.* [2] 41, 289); but its presence is best detected by a mixture of equal volumes of xylidine and glacial acetic acid to which a little alcohol is added when the intense red colour of $C_4H_3O.CH(C_6H_2Me_2NH_2)_2$ is produced: this reaction is exhibited by the product of the distillation of ·00005 g. sugar (H. Schiff, *G.* 17, 355; *B.* 20, 540). Furfuraldehyde may be substituted for sugar in Pettenkofer's reaction; thus a drop of a solution of furfuraldehyde (1 pt.) in water (20,000 pts.) gives a crimson colour on the addition of cholic acid and H_2SO_4. The following substances also give the red colour with H_2SO_4 and furfuraldehyde: isobutyl alcohol, allyl alcohol, *tert*-butyl alcohol, *tert*-amyl alcohol, isoamyl alcohol, oleïc acid, petroleum, acetal, aldehyde, aceto-acetic ether, acetone, glycol, malic acid, alizarin, aniline, anthracene, anthraquinone, atropine, benzoic aldehyde, borneol, pyrocatechin, brucine, quinic acid, cholesterin, cinchonine, codeïne, coniferin, coniine, coumarin, cymene, digitalin, di-methyl-aniline, di-phenyl-amine, gallic acid, cresol, mesitylene, methyl alcohol, methyl-aniline, morphine, naphthalene, (*a*)-naphthol, orcin, paraffin, phenanthrene, phenol, phenyl-hydrazine, phloroglucin, propionic aldehyde, protocatechuic acid, pyrogallol, resorcin, salicylic acid, scatole, stearic acid, strychnine, toluene, thymol, tyrosine, veratrine, and xylene, and (to a slight extent) isopropyl alcohol. The following do not give the red colour: alcohol, propyl alcohol, acetic acid, isobutyric acid, acroleïn, benzene, acetamide, acetophenone, alloxan, aspartic acid, benzonitrile, benzoic acid, succinic acid, pyruvic acid, butyric acid, caffeïne, quinine, quinoline, quinone, quinoxaline, chloral hydrate, chloroform, citric acid, crotonic acid, cyanamide, dextrin, dulcite, fumaric acid, lactic acid, glycerin, glycocoll, glycollic acid, uric acid, urea, hippuric acid, isatin, malic acid, maltose, mandelic acid, mannite, methylamine, oxalic acid, phenylene-*m*-diamine, phenyl-acetic acid, picric acid, piperidine, pyridine, hydroquinone, mucic acid, starch, glucose, tannin, tartaric acid, and cinnamic acid (Mylius, *H.* 11, 492; Udránsky, *H.* 12, 355).

Reactions.—1. When its aqueous solution is boiled with Ag_2O silver is deposited, and silver pyromucate crystallises out of the cooled filtrate.—2. Hot *nitric acid* forms oxalic acid.—3. Cold conc. H_2SO_4 dissolves it unaltered and without becoming coloured; carbonisation sets in on heating.—4. Aqueous KOH, even in the cold, forms resinous products. Alcoholic KOH forms pyromucic acid and furfuryl-carbinol (Ulrich, *C. N.* 3, 116; Limpricht, *Z.* [2] 5, 599). 5. Converted into furoïn $C_{10}H_8O_4$ by heating with aqueous KCy.—6. When mixed with *benzoic aldehyde* (1 equivalent) and treated with KCy it gives benzfuroïn $C_{12}H_{10}O_3$. [139°] (Fischer, *A.* 211, 228).—7. With *nitro-ethane* and aqueous KOH it gives furfuryl-nitro-ethylene $C_4H_3O.CH:CH.NO_2$ [75°] which crystallises in long yellow prisms (Priebs, *B.* 18, 1362).—8. $ZnEt_2$ followed by water forms furfuryl-propyl alcohol $C_4H_3O.CH(OH).C_2H_5$ (180°) (Pawlinoff a. Wagner, *B.* 17, 1968).—9. Condenses with *acetone* in presence of alkalis forming furfuryl-vinyl methyl ketone $C_4H_3O.CH:CH.CO.CH_3$ and di-furfuryl-di-vinyl ketone $(C_4H_3O.CH:CH)_2CO$ (Claisen a. Ponder, *A.* 223, 145).—10. By adding aqueous NaOH to mixed aqueous solutions of furfuraldehyde and *chloro-acetic-aldehyde* there is formed $C_4H_3O.CH:CCl.CHO$ which crystallises in broad yellow needles [79°] sol. hot water, ether, and alcohol. This aldehyde forms a phenyl-hydrazide [157°] and an oxim [165°]; moist Ag_2O oxidises it to *a*-chloro-furfuryl-acrylic acid $C_4H_3O.CH:CCl.CO_2H$ which crystallises in tufts of white needles [142°]. The *a*-chloro-furfuryl-acroleïn is converted by boiling with sodium acetate and silver oxide into $C_4H_3O.CH:CCl.CH:CH.CO_2H$ which forms yellow interlacing needles [168°] (Mehne, *B.* 21, 423).—11. When furfuraldehyde is administered to dogs or rabbits in doses of 5 g. daily little toxic effect is produced; the urine is found to contain pyromucic acid, pyromucuric acid (glycocoll pyromucate) $C_7H_7NO_4$ [165°], and glycocoll furfuryl-acrylate $C_9H_9NO_4$ [215°]. Boiling baryta-water splits up the two last-named compounds into glycocoll and pyromucic or furfuryl-acrylic acids respectively. Fowls are soon killed by taking 1 g. of furfuraldehyde per day; their excreta then contain pyromucornithuric acid $C_{15}H_{16}N_2O_6$ [186°] (Jaffé a. Cohn, *B.* 20, 2311; 21, 3461).—12. A mixture of *pyruvic acid* and *aniline* dissolved in cold ether or alcohol forms the compound $C_{20}H_{16}N_2O_2$ [185°] which crystallises in needles, insol. water, ether, acids, and alkalis, sl. sol. cold, m. sol. hot, alcohol; v. sol. HOAc. This compound gives off aniline when warmed with acids or alkalis (Doebner, *A.* 242, 284).—13. A mixture of pyruvic acid and aniline in warm alcoholic solution forms furfuryl-quinoline carboxylic acid $C_4H_3O.C_9NH_5.CO_2H$ [210°–215°] (Doebner).—14. Furfuraldehyde may be substituted for benzoic aldehyde in Perkin's reaction. Thus with NaOAc and Ac_2O it gives furfuryl-acrylic acid.—15. *Thioglycollic acid* reacts with formation of $C_4H_3O.CH(S.CH_2.CO_2H)_2$ [105°] (Bongartz, *B.* 21, 478).—16. Aqueous *ammonia* in the cold converts furfuraldehyde in a few hours into 'furfuramide' $(C_4H_3O.CH)_3N_2$ [117°] a crystalline body analogous to hydrobenzamide. Boiling aqueous KOH converts furfuramide into a base, furfurine $C_{15}H_{12}N_2O_3$.—17. Combines with secondary and primary *amines* or with 1 mol. of each to form coloured compounds. Thus with mono-methyl-aniline it gives the compound $C_5H_4O_2 2C_6H_5.NHMe$, whose hydrochloride (B'HCl) forms splendid violet crystals [94°] which dissolves to deep-red solutions. With aniline and mono-methyl-aniline it gives $C_5H_4O_2\begin{cases}C_6H_5.NH_2\\C_6H_5.NHMe\end{cases}$. With aniline and tolylene diamine it gives $(C_5H_4O_2)_2\begin{cases}(C_6H_5.NH_2)_2\\C_7H_6(NH_2)_2\end{cases}$. With aniline and benzidine it gives $(C_5H_4O_2)_2\begin{cases}(C_6H_5.NH_2)_2\\C_{12}H_{12}N_2\end{cases}$. The hydrochlorides of these bases crystallise in bronzy metallic crystals which dissolve in alcohol with violet colour. With aniline and amido-benzoic acid or with aniline and naphthylamine-sulphonic acid furfurol yields the compounds:

$C_5H_4O_2\begin{cases}C_6H_5.NH_2\\C_6H_4(NH_2)CO_2H\end{cases}$ and

$C_5H_4O_2\begin{cases}C_6H_5.NH_2\\C_{10}H_6(NH_2)SO_3H\end{cases}$. With the ammonium salt of di-nitro-amido-phenol (picramic acid) it gives $\{C_5H_4O_2\}\{C_6H_2(NO_2)_2(NH_2)(OH)\}$ whose ammonium salt crystallises in glistening golden needles. Weak acids decompose it into its constituents (Schiff, *B.* 19, 847; *cf.* Stenhouse, *A.* 156, 199). Furfuraldehyde combines directly with one equivalent of *m*-amido-benzoic acid, of amido-salicylic acid, and of amido-cuminic acid forming dichroic needles with neutral properties (Schiff, *A.* 201, 355; *G.* 10, 67). The compound of furfuraldehyde with *m*-amido-benzoic acid may be represented on the rosaniline type thus: $C_4H_3O.CH(OH).C_6H_3(CO_2H)NH_2$ (Schiff, *G.* 17, 329).—18. An alcoholic solution of *aniline* (46 pts.) and *aniline hydrochloride* (65 pts.) reacts upon furfurol (48 pts.) forming the hydrochloride of 'furfuraniline' $C_5H_4O_2(NH_2Ph)_2HCl$ (*v. supra*), which crystallises from alcohol in purple needles, insol. water. The free 'furfuraniline' is an unstable brown amorphous mass.—19. *m-Nitro-aniline* forms $C_6H_4(NO_2)NH_2(C_5H_4O_2)$ [100°–120°] which crystallises from alcohol in lemon-yellow crusts. Its hydrochloride $C_{11}H_{10}N_2O_4HCl$ forms copper-coloured plates and gives a crimson solution in alcohol.—20. *Diphenylamine* (2 mols) at 150° forms a compound whose hydrochloride is copper-coloured and forms a crimson solution in alcohol. Diphenylamine hydrochloride gives the same body. 21. *p-Amido-phenol* in dilute aqueous solution reacts with elimination of water, depositing after some time small yellow prisms of 'oxyfurfuraniline' $C_4H_3O.CH{:}N.C_6H_4OH$ [182°] which is sol. alcohol, and forms a hydrochloride that crystallises from alcohol containing NH_4Cl in a form resembling rosaniline hydrochloride (Schiff, *G.* 10, 60; *A.* 201, 358). — 22. *Phenylene-o-diamine hydrochloride* solution forms $(C_4H_3O.CH)_2N_2C_6H_4$ [96°] (Ladenburg a. Engelbrecht, *B.* 11, 1653).—23. *Tolylene-m-diamine* forms $(C_5H_4O_2)_2C_6H_3Me(NH_2)_2$ a crystalline substance, decomposed at 125° without melting. Its hydrochloride forms an intense crimson solution in alcohol, but is much less stable than the corresponding compound with tolylene-*o*-diamine (Schiff; *cf.* Ladenburg, *B.* 11, 595).—24. *Benzidine* in alcoholic solution forms yellow needles of $(C_4H_3O.CH{:}NH)_2C_{12}H_8$; which gives a hydrochloride crystallising in copper-coloured scales, and a platinochloride separating as a yellow crystalline powder.—25. When triturated with *m-amido-benzoic acid* it combines to form $(C_5H_4O_2)C_6H_4(NH_2).CO_2H$ which crystallises in small dichroic scales resembling a salt of rosaniline. Its hydrochloride forms red velvety crystals and gives crimson solutions in alcohol and HOAc. It dissolves in Na_2CO_3Aq without evolution of CO_2.—26. A mixture of *aniline hydrochloride* and *methyl-aniline* give a ruby-red colouration turning green and finally violet; the body formed in this reaction $C_5H_4O_2(NH_2Ph)(NHMePh)HCl$ is a crystalline mass, v. sol. alcohol, insol. water.—27. (β)-*Naphthylamine* forms, with elimination of water, $C_4H_3O.CH{:}N.C_{10}H_7$ [85°]. It crystallises from alcohol in colourless scales. Its hydrochloride B'HCl forms yellow needles dissolving in alcohol with a deep red colour (Schiff, *G.* 17, 340).—28. *Di-methyl-aniline* and $ZnCl_2$ heated with furfuraldehyde form $C_{21}H_{24}N_2O$ [83°] which crystallises from ligroïn in needles. It forms a crystalline platinochloride $B''H_2PtCl_6$ and picrate $B''(C_6H_2(NO_2)_3OH)_2$ (Fischer, *A.* 206, 141).—29. (*Py.*3)-*Methyl-quinoline* heated with an equivalent of furfuraldehyde at 100° together with a small quantity of $ZnCl_2$ forms a base $C_{15}H_{11}NO$ which crystallises from ligroïn in needles or tables that turn black in daylight. Its salts B'HCl, $B'HNO_3$, $B'H_2SO_4$ aq, $B'_2H_2PtCl_6$ 2aq, and $B'C_6H_2(NO_2)_3OH$ are crystalline (Srpek, *B.* 20, 2044).—30. *Carbamic ether* in presence of HCl forms $C_4H_3O.CH(NH.CO_2Et)_2$ [169°] which may be sublimed as long thin needles, insol. water, v. e. sol. alcohol and ether (Bischoff, *B.* 7, 1081). 31. A solution of *urea nitrate* is coloured violet by furfuraldehyde and the solution gradually deposits a black substance (Schiff, *B.* 10, 773).—32. *Ammonium sulphide* forms thiofurfuraldehyde $C_4H_3O.CHS$ (Cahours, *A. Ch.* [3] 24, 281), which is a yellow crystalline powder. When heated thiofurfuraldehyde gives off an unpleasant odour and yields a sublimate of a polymeride of furfuraldehyde [98°] (Schwanert, *A.* 184, 61).—33. With benzil and alcoholic NH_3 it forms two compounds of the formula $C_{24}H_{20}N_2O_4$ [246°] and [above 300°] (Japp a. Hooker, *C. J.* 45, 684).—34. With phenanthraquinone and NH_3 it gives $C_{14}H_8{<}{}^{O}_{N}{>}C.C_4H_3O$ [231°] (Japp a. Wilcock, *C. J.* 39, 217).

Combination. $C_4H_3O.CH(OH).SO_3Na$. Formed by adding alcohol to a solution of furfuraldehyde in conc. $NaHSO_3Aq$. White laminæ, with fatty lustre.

Oxim $C_4H_3O.CH{:}NOH$. [89°]. (201°-208°). Formed by the action of hydroxylamine (base) on furfuraldehyde (Odernheimer, *B.* 16, 2988). Long thin white needles. By heating with HCl it is resolved into its constituents. Salts.—$C_5H_4O.NOH,HCl$: white crystalline powder, sol. water and alcohol.—$C_5H_4O.N(ONa)$ 3aq: white scales. It gives characteristic pps. with the salts of the heavy metals.

Ethyl ether $C_5H_4O.N(OEt)$: colourless liquid, volatile with steam, lighter than water, in which it is slightly soluble.

Phenyl hydrazide $C_4H_3O.CH{:}N.NHC_6H_5$. [98°]. Formed by adding a solution of phenylhydrazine hydrochloride (*q.v.*) and sodium acetate to an aqueous solution of furfuraldehyde; 1 pt. of furfuraldehyde in 10,000 pts. of water gives a distinct crystalline pp. (Fischer, *B.* 17, 574). Fine colourless plates. Insol. water, sol. ether, from which solution it is ppd. in crystals by adding ligroïn.

Di-phenyl-hydrazide $C_4H_3O.CH(NPh)_2$. [59°] (Cornelius a. Homolka, *B.* 19, 2240).

FURFURAMIDE $C_{15}H_{12}N_2O_3$ *i.e.* $(C_5H_4O)_3N_2$. [117°]. Formed as a crystalline mass by allowing furfuraldehyde to stand for some hours with (5 times its volume of) conc. NH_3Aq (Fownes, *Tr.* 1845, 253; *A.* 54, 55; R. Schiff, *B.* 10, 1188). Tufts of needles (from alcohol). Insol. cold water, v. sol. alcohol and ether. When heated with water it is slowly resolved into ammonia and furfuraldehyde; this change is instantly produced by acids. H_2S yields thiofurfuraldehyde (*v. supra*). Boiling dilute KOH converts furfuramide into the isomeric furfurine. When heated with an alcoholic solution of phenyl thiocarbimide it forms a crystalline compound $C_{22}H_{19}N_3SO_4$, insol. water, sl. sol. cold alcohol.

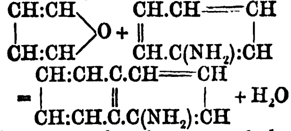
FURFURANE C_4H_4O. *Furane. Tetraphenol. Tetrol. Tetrane.* (31°). V.D. 2·4. S.G. ^{0} ·964; ^{15} ·944. Formed by distilling barium pyromucate with soda-lime (Rohde, *B.* 3, 90; Limpricht, *A.* 165, 281). Formed also by the action of PCl_5 on its dihydride. The product is washed with KOHAq, dried by K_2CO_3, and rectified (Henninger, *A. Ch.* [6] 7, 222). It is a liquid. Unacted upon by KHO, aniline, or hydroxylamine. Colours pine-wood moistened with HCl emerald green (Canzoneri a. Oliveri, *G.* 16, 490). HCl converts it into a yellow-black compound. PCl_5 forms with it a black compound. With Br, C_4H_3OBr, and $C_4H_2OBr_2$ [5°] (65°) at 30 mm. are formed.

Furfurane dihydride C_4H_6O. (67°). S.G. ^{0} ·967; ^{15} ·95. V.D. 2·35.

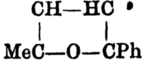
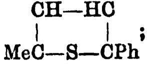
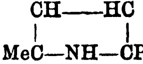
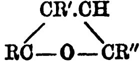
Preparation.—A product of the action of formic acid on erythrite. Separated from the crotonic aldehyde, which is also formed, by fractional distillation (Henninger, *A. Ch.* [6] 7, 218).

Properties.—Very stable liquid; does not blacken nor polymerise. Forms a dibromide $C_4H_6Br_2O$. [12°]. (95° at 30 mm.). Yields furfurane (31°) when heated with PCl_5. Conc. HI and yellow phosphorus give *sec*-butyl iodide (120°).

Derivatives of furfurane. — Furfurane $(C_4H_4)O$ is the oxygen analogue of thiophene $(C_4H_4)S$ and pyrrole $(C_4H_4)NH$, and all three compounds are doubtless constituted in an analogous manner. Since in their reactions they resemble benzene and its derivatives rather than the fatty group, it is generally held that their molecules should be represented by ring formulæ. When pyromucic acid is distilled with lime and ammonia-zinc chloride, it yields pyrrole as well as furfurane. In this reaction we may suppose the O of the furfurane directly displaced by NH (Canzoneri a. Oliveri, *G.* 16, 486). When a mixture of pyromucic acid, aniline, and $ZnCl_2$ is heated (α)-naphthylamine is produced. In this reaction the (nascent) furfurane acts (like an alcohol, phenol, or glycide) as if it were the anhydride of the alcohol CH(OH):CH.CH:CH(OH), the reaction being:



$$\begin{matrix}CH:CH\\ |\\ CH:CH\end{matrix}\!\!>\!O + \begin{matrix}CH.CH=\!\!=CH\\ \|\qquad\quad |\\ CH.C(NH_2):CH\end{matrix} = \begin{matrix}CH:CH.C.CH=\!\!=CH\\ |\qquad\quad \|\qquad |\\ CH:CH.C.C(NH_2):CH\end{matrix} + H_2O$$

(C. a. O.). As another instance of the analogy of furfurane with thiophene and pyrrole, we may take the condensation of acetophenone-acetone $Ph.CO.CH_2.CH_2.CO.Me$ or the alternative Ph.C(OH):CH.CH.C(OH).Me, which by treatment with P_2O_5 loses H_2O, giving phenyl-methyl-furfurane  $\begin{matrix}CH—HC\\ |\qquad |\\ MeC—O—CPh\end{matrix}$. In an analogous manner, when heated with P_2S_5, it gives phenyl-methyl-thiophene  $\begin{matrix}CH—HC\\ |\qquad |\\ MeC—S—CPh\end{matrix}$; and with alcoholic NH_3 it gives phenyl-methyl-pyrrole  $\begin{matrix}CH—HC\\ |\qquad |\\ MeC—NH—CPh\end{matrix}$ (Paal, *B.* 18, 367). Just as $Ph.CO.CH_2.CH_2.CO.Me$ yields a furfurane derivative by condensation, so acetonyl-acetone $MeCO.CH_2.CH_2.CO.Me$, di-acetyl-succinic ether $Me.CO.CH(CO_2Et).CH(CO_2Et).CO.Me$, acetonyl-aceto-acetic ether $Me.CO.CH_2.CH(CO_2Et).CO.Me$, and di-tolyl-ethylene $C_7H_7.CO.CH_2.CH_2.CO.C_7H_7$ yield corresponding derivatives of furfurane. Diketones of the form $RCO.CR'(OH).CH_2.CO.R''$ and R.CO.CR′:CH.CO.R″ yield on reduction furfurane derivatives  $\begin{matrix}CR'.CH\\ /\qquad \backslash\\ RC—O—CR''\end{matrix}$ (Japp a. Klingemann, *B.* 21, 2932).

Furfurane being analogous to benzene, the radicle C_4H_3O will resemble phenyl in its general character. Baeyer proposed to call this radicle 'furfur'; but it is called furfuryl in this Dictionary.

References.— Benzo-di-methyl-di-furfurane di-carboxylic acid, vol. i. p. 478; Bromo-furfurane, vol. i. p. 572; Di-methyl-furfurane, Methyl-furfurane carboxylic acids, Di-phenyl-furfurane and its carboxylic acid, Phenyl-methyl-furfurane and its carboxylic acid, Phenyl-di-methyl-furfurane di-carboxylic ether, vol. i. p. 495; Di-tolyl-furfurane, and Pyromucic acid.

FURFURANE-CARBOXYLIC ACID *v.* Pyromucic acid.

Furfurane di-carboxylic acid *v. Dehydro*-mucic acid.

FURFURANGELIC ACID *v.* Furfuryl-angelic acid.

FURFURBUTYLENE *v.* Furfuryl-butylene.

FURFUR-CROTONIC ACID *v.* Furfuryl-crotonic acid.

FURFUR-CYANIDE *v. Nitrile* of Pyromucic acid.

FURFURINE $C_{15}H_{12}O_3N_2$. [116°]. S. ·75 at 100°; ·021 at 8°.

Preparation.—Furfuraldehyde, obtained by distilling bran with dilute H_2SO_4, is converted by strong NH_3 into furfuramide. Furfuramide is boiled with very dilute KOH for 10 minutes, on cooling furfurine separates as slender needles. These are boiled with excess of oxalic acid, the solution is decolourised by animal charcoal and allowed to crystallise. The acid oxalate then separates. It is decomposed by NH_3 (Bahrmann, *J. pr.* [2] 27, 311; *cf.* Fownes, *Tr.* 1845, 253; Stenhouse, *A.* 74, 289; Svanberg a. Bergstrand, *J. pr.* 66, 239; Bertagnini, *A.* 88, 128).

Properties.—Soft white silky needles. Permanent in the air when dry, but turns brown when exposed to moist air. Sl. sol. water, v. e. sol. alcohol and ether. Its solutions exhibit alkaline reaction.

Reactions.—1. *Acetyl chloride* added to an ethereal solution of furfurine appears to form a molecular compound, which, however, is decomposed by alcohol into furfurine hydrochloride and acetyl furfurine, thus: $2C_{15}H_{12}O_3N_2 + AcCl = C_{15}H_{12}O_3N_2,HCl + C_{15}H_{11}AcO_3N_2$. — 2. *Benzoyl chloride* appears also to form an unstable molecular compound, it is decomposed by warm alcohol, and the product may be $C_{15}H_{10}(OEt)BzO_3N_2$. 3. *Chloroformic ether*, $ClCO_2Et$, added to an ethereal solution of furfurine, forms furfurine carboxylic ether: $C_{15}H_{11}(CO_2Et)O_3N_2$ [124°] (Bahrmann, *J. pr.* [2] 27, 311).—4. *Furfurine* separates iodine from aqueous periodic acid (Bödeker, *A.* 71, 64). - 5. A very dilute solution of KNO_2, added to one of furfurine sulphate, gives a pp. of the nitrosamine $C_{15}H_{11}(NO)N_2O_3$ which separates from ether in golden triclinic crystals [112°] insol. water, m. sol. alcohol and ether (R. Schiff, *B.* 11, 1250). But if the solution of furfurine sulphate be not very dilute, a compound $C_{30}H_{27}N_5O_{15}$ [95°] separates after some time. This is yellow and crystalline, and is also formed by saturating an alcoholic solution of furfurine sulphate with nitrous gas. It is insol. water and ether, v. sol. alcohol, and forms a platinochloride $(C_{30}H_{27}N_5O_{15})_2H_2PtCl_6$.

Salts.—Furfurine expels NH_3 from boiling aqueous NH_4Cl, but is itself ppd. by NH_3 from its salts in the cold. The salts of furfurine have an extremely bitter taste. They are ppd. by $HgCl_2$ and by H_2PtCl_6.—B′HCl aq: tufts of silky needles, v. sol. water, m. sol. HClAq. Neutral in reaction. Does not effloresce over H_2SO_4.—$B'_2H_2PtCl_6$: long light-yellow needles.—B′HI aq: slender, oblique, four-sided prisms. S. 18 in the cold.—B′HBr aq: short prismatic needles. S. 3·9 (Davidson, *Ed. N. Phil. J.* [2] 2, 284).—$B'_2H_2Cr_2O_7$: orange-yellow powder, sl. sol. cold water (D.).—$B'HNO_3$: trimetric prisms (from alcohol).—$B'HClO_4$ aq: long thin trimetric prisms [150°–160°]. Effloresces at 60°. V. sol. water and alcohol (Bödeker, *A.* 71, 63; Dauber, *A.* 71, 67).—$B'H_2SO_4$ 3½aq: prisms, v. sol. water, m. sol. alcohol and ether, sl. sol. dilute H_2SO_4. Efflorescent.—$B'H_3PO_4$: four-sided trimetric laminæ. [200°–215°]. V. sol. hot water and alcohol, insol. ether.—$B'_2H_3PO_4$: glittering, oblique, four-sided prisms: v. sol. boiling water and alcohol, nearly insol. ether. Neutral in reaction.—$B'_3H_3PO_4$: long, oblique, four-sided prisms without lustre; permanent in the air; v. sol. water and alcohol, sl. sol. ether. Has an alkaline reaction.—$B'_4H_4P_2O_7$ aq: glassy crystalline crust; v. sol. water and alcohol; neutral in reaction.—$B'H_2C_2O_4$: thin tables, v. sl. sol. cold water.

Acetyl derivative $C_{15}H_{11}AcN_2O_3$. [c. 250°]. From furfurine and Ac_2O by gently warming (R. Schiff, *B.* 10, 1188). White flocculent micro-crystalline mass (from boiling alcohol). Insol. water, m. sol. alcohol and ether. Not saponified by boiling aqueous KOH. Does not combine with acids. With bromine in HOAc it forms a hexabromide $C_{15}H_{11}Br_6AcN_2O_3$ which is ppd. on adding water.

Ethyl-furfurine $C_{15}H_{11}EtN_2O_3$. The hydriodide is formed by heating an alcoholic solution of furfurine with EtI at 100° (Davidson). It separates by evaporation of the cold alcoholic solution in prisms. S. 2·8. M. sol. alcohol and ether. Moist Ag_2O converts it into a syrupy alkaline hydroxide which forms a platinochloride $(C_{15}H_{11}EtN_2O_3)_2H_2PtCl_6$.

Isoamyl furfurine $C_{15}H_{11}(C_5H_{11})N_2O_3$. The hydro-iodide prepared by heating furfurine with isoamyl iodide is a radio-crystalline mass. The platinochloride $B'_2H_2PtCl_6$ is a yellow powder, sl. sol. water.

FURFURO-BENZIDINE *v.* FURFURALDEHYDE, *Reaction* 23.

FURFUROL *v.* FURFURALDEHYDE.

FURFURO-(β)-NAPHTHYLAMINE *v.* FURFURALDEHYDE, *Reaction* 26.

FURFURONITRILE *v.* *Nitrile* of PYROMUCIC ACID.

FURFURYL-ACROLEÏN *v.* FURFURYL-ACRYLIC ALDEHYDE.

FURFURYL-ACRYLIC ACID $C_7H_6O_3$ *i.e.* $C_4H_3O.CH:CH.CO_2H$. *Furfuracrylic acid.* [136°]. S. ·2 (in the cold). Formed, by Perkin's reaction, by heating furfuraldehyde (1 pt.) with NaOAc (2 pts.) and Ac_2O (2 pts.) at 250° for 11 hours; the solution solidifies on cooling, and after dissolving in Na_2CO_3Aq, the acid is ppd. by HCl. The yield is 80 p.c. of the theoretical (Baeyer, *B.* 10, 355; Marckwald, *B.* 20, 2811). Formed also by oxidation of the corresponding aldehyde, furfuryl-acrylic aldehyde, by Ag_2O (J. G. Schmidt, *B.* 13, 2344). Formed, together with glycocoll, by the action of boiling baryta-water on furfuryl-acryluric acid, which is in the urine of dogs that have taken furfuraldehyde (*q.v.*). Long white needles (from water); volatile with steam. The Ag salt is m. sol. hot water.

Reactions.—1. Reduced by *sodium-amalgam* to furfuryl-propionic acid.—2. *Bromine* acting on furfuryl-acrylic acid forms crystalline $C_7H_5Br_3O_3$, which is decomposed by water into di-bromo-furfuryl-ethylene and CO_2 (Hill, *B.* 20, 3359).—3. When furfuracrylic acid is heated with 95 p.c. *alcohol* (3·5 pts.) and saturated with HCl there is formed an ether $C_5H_8O(CO_2Et)_2$ (286°), possibly $(CO_2Et.CH_2.CH_2)_2CO$ (since it forms a phenyl hydrazide [115°] and an oxim [38°]); it is a heavy oil, and the corresponding acid forms thin prisms [138°], and has a crystalline silver salt. The acid $C_5H_8O(CO_2H)_2$ does not combine with Br, is not reduced by sodium-amalgam, and yields succinic acid when oxidised by HNO_3 (Marckwald, *B.* 20, 2811; 21, 1398). The acid ether $C_5H_8O(CO_2H)(CO_2Et)$ [68°] forms a crystalline oxim [112°].

Ethyl ether EtA'. (229°). Oil.

α-Chloro-furfuryl-acrylic acid $C_4H_3O.CH:CCl.CO_2H$. [142°]. Prepared by digesting α-chloro-furfuryl-acroleïn with Ag_2O.

Properties.—Rosettes of white crystals, sol. hot water, alcohol, ether, benzene, and chloroform, insol. light petroleum. It agglomerates before melting. Conc. H_2SO_4 gives a red colour changing to yellow on dilution.

Salts.—Cu salt is a greenish pp. dissolving in ammonia with blue colour.—Pb and Hg salts are white pps., sol. hot water.—Fe salt is a red-brown pp.—Zn salt a white gelatinous pp.—Alkaline and alkaline earth salts are v. sol. water (P. Mehne, *B.* 21, 426).

FURFURYLACRYLIC ALDEHYDE $C_7H_6O_2$ *i.e.* $C_4H_3O.CH:CH.CHO$. [51°]. (above 200°). Prepared by the action of aldehyde or paraldehyde and aqueous KOH on furfurol (Schmidt, *B.* 13, 2342). Very volatile with steam. Long colourless needles. V. sol. hot, sl. sol. cold, water.

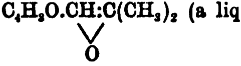
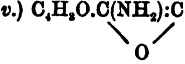
Reactions.—With aniline dissolved in acetic acid it gives an intense green colouration. Reduces Ag_2O forming furfurylacrylic acid.

α-Chloro-furfuryl-acrylic aldehyde $C_4H_3O.CH:CCl.CHO$. [79°]. From furfuraldehyde, chloro-acetic aldehyde, and aqueous NaOH (Mehne). Broad yellow needles, sol. hot water, ether, and alcohol. Forms a phenyl-hydrazide [157°] and an oxim [165°].

FURFURYLAMINE *v.* FURFURYL-CARBINYL AMINE.

FURFURYL-ANGELIC ACID $C_9H_{10}O_3$ *i.e.* $C_4H_3O.CH:CEt.CO_2H$. [88°]. Formed by gradually heating furfuraldehyde with *n*-butyric anhydride and sodium *n*-butyrate in an open vessel to 180° (Baeyer, *B.* 10, 1364; Tönnies, *B.* 12, 1200). Silky needles (from hot water). Reduced by sodium-amalgam to furfuryl-valeric acid.

FURFURYL-BUTYLENE $C_4H_3O.CH:C(CH_3)_2$. (153°). V.D. = 4·27. S.G. $\frac{14}{14}$ = ·9509. Prepared by cohobating a mixture of furfuraldehyde (3 pts.), isobutyric anhydride (7 pts.) and fused sodium acetate (4 pts.) for twelve hours. Sodium isobutyrate used instead of acetate gives the same product.

Addition product with N_2O_3. — $C_8H_{10}O_4N_2$ [94°]; large glistening tables; easily soluble in ordinary solvents. It decomposes at 145°–150° into its constituents. On reduction with tin and HCl it gives a mixture of furfurylbutylene oxide  $C_4H_3O.\underbrace{CH:C}_{O}(CH_3)_2$ (a liquid (186°), sol. water and volatile with steam) and amido-furfurylbutylene oxide (*q.v.*)  $C_4H_3O.\underbrace{C(NH_2):C}_{O}(CH_3)_2$ (Tönnies a. Staub, *B.* 17, 851; *cf.* *B.* 11, 1511).

FURFURYL-CARBINOL $C_5H_6O_2$ *i.e.* $C_4H_3O.CH_2OH$. Formed by reducing furfuraldehyde with sodium-amalgam (Beilstein a. Schmelz, *A. Suppl.* 3, 275). Formed also, together with pyromucic acid, by the action of alcoholic KOH on furfuraldehyde (Limpricht, *Z.* [2] 5, 599). Syrup drying up to an amorphous resin; cannot be distilled. HClAq colours it green. Gives succinic acid, HOAc, formic acid, and CO_2 on fusion with KOH. Aniline added to its aqueous solution gives a yellow flocculent pp. of $C_{11}H_{11}NO$. Aniline hydrochloride added to its alcoholic solution ppts. reddish-green scales of $C_{11}H_{11}NO,NH_2PhHCl$ (H. Schiff, *B.* 19, 2154).

FURFURYL-CARBINYL-AMINE $C_4H_3O.CH_2.NH_2$. (146°) (C. a. D.); (135°) (T.). V.D. = 49·1 (obs.). Prepared by reduction of pyromuco-nitrile with zinc and dilute H_2SO_4. The product is distilled with steam, the distillate acidified and evaporated to a small bulk; on adding solid KOH the base separates (Ciamician a. Dennstedt, *B.* 14, 1475; *G.* 11, 332). Obtained also by reducing the phenyl-hydrazide of furfuraldehyde (45 g.) dissolved in alcohol (600 g.) with 2½ p.c. sodium-amalgam (1350 g.) in the cold (below 3°) (Tafel, *B.* 20, 398). Liquid. Miscible with water. Strong smell. Powerful base. Absorbs CO_2 from the air forming a crystalline mass [75°].

Salts.—B'HCl: colourless soluble prisms or needles. $(B'HCl)_2PtCl_4$: orange-yellow trimetric plates, soluble in hot water, sparingly in cold.—$B'H_2C_2O_4$ ½aq: narrow scales.—The sulphate forms minute needles.—The picrate forms golden prisms decomposing at 150° without fusion.

FURFURYL-CROTONIC ACID $C_8H_8O_3$ *i.e.* $C_4H_3O.CH:CMe.CO_2H$. [107°]. Formed by oxidising the corresponding aldehyde with Ag_2O (J. G. Schmidt, *B.* 14, 575). Glittering plates (from hot water) or slender needles (by sublimation). Conc. H_2SO_4 forms with it a red solution.

FURFURYL-CROTONIC ALDEHYDE $C_8H_8O_2$ *i.e.* $C_4H_3O.CH:CMe.CHO$ (?) (120° at 110 mm.). Prepared by adding NaOH to an aqueous solution of propionic aldehyde and furfuraldehyde (J. G. Schmidt, *B.* 14, 574). Colourless liquid. Volatile with steam. Gives a green colouration with aniline and acetic acid, and a yellow passing into violet with magenta decolourised with SO_2. By Ag_2O it is oxidised to furfuryl-crotonic acid.

FURFURYL-ETHYL-CARBINOL *v.* FURFURYL-PROPYL ALCOHOL.

FURFURYL-ETHYL-PYRIDINE

Hexahydride $C_4H_3O.CH_2.CH_2.C_5H_{10}N$. (246°). From furfuryl-vinyl-pyridine and sodium in presence of alcohol (Merck, *B.* 21, 2709).—B'HCl: [145°-148°].—B'HBr. [c. 135°].—B'HI. [c. 121°].

FURFURYLIDENE-ACETONE *v.* FURFURYL-VINYL METHYL KETONE.

FURFURYL-METHYLENE-DI-CARBAMIC ETHER $C_4H_3O.CH(NH.CO_2Et)_2$. [169°]. Separates immediately on adding a drop of HClAq to a mixture of furfuraldehyde and carbamic ether (Bischoff, *B.* 7, 1081). Silky needles (from alcohol); insol. water, v. sol. alcohol and ether.

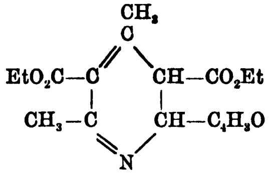
FURFURYL-METHYLENE-MALONIC ACID $C_4H_3O.CH:C(CO_2H)_2$. [187°]. From its ether. Prisms (from ether, alcohol, or HOAc); v. sol. water, insol. benzene, light petroleum, and chloroform. Split up by heat into CO_2 and furfuryl-acrylic acid. Reduced by sodium-amalgam to furfuryl-isosuccinic acid.

Mono-ethyl ether EtHA''. [103°]. Formed by gently heating the diethyl ether with potash. Trimetric prisms (from benzene). V. sl. sol. cold, m. sol. hot, water, m. sol. benzene and chloroform, insol. light petroleum. Split up by distillation into CO_2 and furfuryl-acrylic acid.

Di-ethyl ether Et_2A''. Formed by heating a mixture of furfuraldehyde and malonic ether with Ac_2O (Marckwald, *B.* 21, 1080). Oil; miscible with alcohol.

Amide $C_4H_3O.CH:C(CONH_2)_2$. [180°]. Needles (from alcohol); m. sol. hot water, v. e. sol. HOAc, insol. ether.

FURFURYL-DI-METHYL-PYRIDINE-DI-HYDRIDE DI-CARBOXYLIC ETHER $C_{17}H_{21}NO_5$

or  [164°]. Formed by heating a mixture of furfuraldehyde and aceto-acetic ether with alcoholic NH_3. Colourless crystals. On oxidation it gives furfuryl-di-methyl-pyridine di-carboxylic acid (R. Schiff a. Puliti, *B.* 16, 1608).

FURFURYL-NITRO-ETHYLENE $C_4H_3O.CH:CH(NO_2)$. [75°]. Formed by the action of furfuraldehyde upon an alkaline solution of nitromethane (Priebs, *B.* 18, 1362). Long yellow prisms. Easily volatile with steam. Gives on nitration $C_4H_2(NO_2)O.CH:CH(NO_2)$ [144°] which forms a crystalline dibromide [111°] and is oxidised by CrO_3 to nitro-pyromucic acid.

FURFURYL-PROPIONIC ACID $C_4H_3O.CHMe.CO_2H$. [51°]. From furfuryl-acrylic acid by sodium amalgam (Baeyer, *B.* 10, 357). Sol. water and ether. Coloured yellow by HCl. Converted into furonic acid by successive treatment with Br and Ag_2O.

Amide $C_4H_3O.CHMe.CONH_2$. [98°]. (270°). Formed by heating the ammonium salt in a closed tube for some hours at 220° (Marckwald, *B.* 20, 2811). Needles, sol. water, alcohol, ether, and benzene, sl. sol. light petroleum.

FURFURYL-PROPYL ALCOHOL $C_4H_3O.CH(OH).C_2H_5$. *Furfuryl-ethyl-carbinol.* (180° at 750 mm.). S.G. $\frac{0}{0}$ 1·066; $\frac{16}{0}$ 1·053. Formed by the action of zinc ethyl on furfuraldehyde and treatment of the product with water. Thick liquid (Pawlinoff a. Wagner, *B.* 17, 1968).

(*Py.* 3)-**FURFURYL-QUINOLINE** $C_9H_6NC_4H_3O$. [92°]. (above 300°). Formed by heating its carboxylic acid above its melting-point (Döbner, *A.* 242, 287). Long needles. Insol. cold, v. sl. sol. hot, water, v. e. sol. other ordinary solvents.

Salts.—$(B'HCl)_2PtCl_4$ 2aq: small yellow needles; sl. sol. cold, v. sol. hot, water.—$B'HClAuCl_3$: lemon-yellow needles; sol. hot water.—$B'H_2Cr_2O_7$: orange-red needles; sol. hot water.—Picrate: [186°]; large yellow plates.

(*Py.* 3)-**FURFURYL-QUINOLINE** (*Py.* 1)-**CARBOXYLIC ACID** $C_9H_5N(C_4H_3O)CO_2H$. (*Py.* 3)-*Furfuryl-cinchonic acid.* [c. 215°]. Formed by heating together furfuraldehyde, pyruvic acid, and aniline in alcoholic solution (Döbner, *A.* 242, 285). Greenish-yellow needles. Sl. sol. cold, v. sol. hot water, v. e. sol. alcohol, ether, and benzene. Heated above its melting-point it yields (*Py.* 3)-furfuryl-quinoline.

Salts.—The Ag, Pb, and Cu salts are sl. sol. water. The chloride, nitrate, and sulphate, are v. sol. water.—$(B'HCl)_2PtCl_4$: orange-yellow needles; sl. sol. cold, v. sol. hot, water.—$(B'HCl)_2AuCl_4$: lemon-yellow needles.

FURFURYL-ISOSUCCINIC ACID $C_4H_3O.CH_2.CH(CO_2H)_2$. [125°]. Formed by reducing furfuryl-methylene-malonic acid with sodium-amalgam (Marckwald, *B.* 21, 1080). Long slender needles, v. sol. water, ether, HOAc, and alcohol; almost insol. light petroleum. Split up by distillation into CO_2 and furfuryl-propionic acid.

FURFURYL-VALERIC ACID $C_9H_{12}O_3$ *i.e.* $C_4H_3O.CH_2.CHEt.CO_2H$. Formed by reducing furfuryl-angelic acid by sodium-amalgam (Baeyer a. Tönnies, *B.* 10, 1364; 12, 1200). Oil. By successive treatment with Br and Ag_2O it is converted into 'butyro-furonic acid' $C_9H_{12}O_5$.

DI-FURFURYL-DI-VINYL KETONE $(C_4H_3O.CH:CH)_2CO$. *Di-furfural-acetone.* [61°]. From furfuraldehyde (20 g.), acetone (6 g.), water (400 g.), alcohol (300 c.c.), and NaOH (3 g.) dissolved in water (27 g.). Flat lemon-yellow prisms, turning brown in air. V. sol. alcohol, ether, and chloroform, less sol. light petroleum. With conc. H_2SO_4, AcCl, or fuming HCl it gives dark-red solutions (Claisen a. Ponder, *A.* 223, 146).

FURFURYL-VINYL METHYL KETONE $C_4H_3O.CH:CH.CO.Me$. *Furfural-acetone.* [40°]. (135°–137°) at 34 mm.; (229°) at 760 mm. From furfuraldehyde (20 g.), acetone (30 g.), water (1000 g.), and dilute (10 p.c.) NaOH (30 g.) left 24 hours in the cold, then extracted with ether and distilled. Yellow oil, smelling of cinnamon and of furfuraldehyde, but soon solidifies to thick prisms. V. sol. alcohol, ether, and chloroform, less sol. petroleum. In H_2SO_4 it forms a brownish-yellow colour turning wine-red on heating. AcCl forms an orange liquid turning emerald-green (Claisen a. Ponder, *B.* 14, 2468; *A.* 223, 145; J. G. Schmidt, *B.* 14, 1459).

FURFURYL-(*Py.* 3)-VINYL-PYRIDINE $C_4H_3O.CH:CH.C_5H_4N$. [51°–53°]. From furfuraldehyde and (*a*)-methyl-pyridine at 165° in presence of a little $ZnCl_2$ (Merck, *B.* 21, 2709). Needles (from water); blackens in air; v. sol. alcohol and ether.—$B\,HHgCl_3aq$ [133°].—$B'_2H_2PtCl_6 2aq$. [155°].—$B'C_6H_2(NO_2)_3OH$. [185°–190°]; yellow needles.

FURFURYL-VINYL STYRYL KETONE $C_4H_3O.CH:CH.CO.CH:CH.Ph$. *Furfural-benzylidene-acetone.* [56°]. From benzylidene-acetone (10 g.) and furfuraldehyde (7 g.), or from furfural-acetone (10 g.) and benzoic aldehyde (8 g.) in presence of water (200 g.), alcohol (130 g.), and dilute (10 p.c.) NaOH (10 g.).

Properties.—Straw-yellow plates (from boiling light petroleum). V. sol. alcohol, ether, benzene, and chloroform, less sol. petroleum. Conc. H_2SO_4 forms a dark red, AcCl an orange solution (Claisen a. Ponder, *A.* 223, 147).

FURIL $C_{10}H_6O_4$ *i.e.* $C_4H_3O.CO.CO.C_4H_3O$. [162°]. Prepared by passing a stream of air through a solution of furoin in alcoholic NaOH (E. Fischer, *B.* 13, 1337; *A.* 211, 221). Yellow needles. Insol. water, sl. sol. alcohol and ether, v. sol. chloroform. By sodium-amalgam it is reduced to furoïn. By aqueous KOH(1:2) it is converted into furilic acid. According to Jourdain (*B.* 16, 659) alcohol containing a little KCy gives furfuraldehyde and pyromucic ether.

Furil-octo-bromide $C_{10}H_6O_4Br_8$. [185°]. Crystalline. Sl. sol. alcohol, m. sol. chloroform. Prepared by the action of an excess of bromine on furil. On fusion it evolves Br and HBr, forming dibromo-furil and a small quantity of bromo-furil.

Bromo-furil $C_{14}H_5BrO_4$. [110°]? Yellow plates.

Di-bromo-furil $C_{10}H_4Br_2O_4$. [184°]. Sublimable. Golden yellow plates.

Benz-furil *v.* vol. i. p. 462.

FURILIC ACID $(C_4H_3O)_2C(OH).CO_2H$. Formed by rubbing furil with warm KOHAq, adding dilute H_2SO_4, filtering from a separated resin, and extracting the filtrate with ether (E. Fischer, *A.* 211, 220). Unstable needles; decomposed at 100°; m. sol. cold water, v. sol. alcohol and ether. A resin slowly separates from the aqueous solution.

Di-bromo-furilic acid $C_{10}H_6Br_2O_5$. Formed by the action of baryta-water on di-bromo-furil. Its alcoholic solution is turned red by warming after addition of some dilute H_2SO_4.—BaA'_2: slender needles.

FUROÏN $C_{10}H_8O_4$. [135°]. Prepared by boiling furfuraldehyde (40 g.), alcohol (30 g.), water (80 g.), and potassium cyanide (4 g.) for half an hour in a flask with inverted condenser. Crystallised from toluene or alcohol (E. Fischer, *A.* 211, 218; *B.* 13, 1334). Prisms. Distils unchanged. Sl. sol. hot water, alcohol, and ether. Conc. H_2SO_4 forms a bluish-green colour. Weak acid. Gives an absorption spectrum. The solution in alcoholic NaOH is bluish-green, and is oxidised by the air to furil.

Acetyl derivative $C_{10}H_7AcO_4$. [76°]. Needles.

FURONIC ACID $C_7H_8O_5$. [180°]. Formed by adding bromine (1 mol.) to an aqueous solution of furfuryl-propionic acid (1 mol.), and treating the product with Ag_2O (6 mols.) (Baeyer, *B.* 10, 696, 1358). Colourless needles (from hot water). Sl. sol. cold water and ether. Conc. H_2SO_4 forms a reddish-yellow solution. HClAq is not coloured by it. Hydriodic acid and red phosphorus at 200° reduce it to *n*-pimelic acid $CO_2H.CH_2.CH_2.CH_2.CH_2.CH_2.CO_2H$? Sodium-amalgam gives hydrofuronic acid $C_7H_{10}O_5$.—Ag_2A''.

Hydrofuronic acid $C_7H_{10}O_5$. [112°]. Formed as above. Needles.—Ag_2A'': m. sol. hot water.

FUSCO-SCLEROTIC ACID $C_{14}H_{24}O_7$. An acid extracted by Dragendorff (*C. C.* 1878, 125, 141) from ergot by ether, the ergot having previously been treated with a solution of tartaric acid. It may be separated from 'picrosclerotic acid' by H_2SO_4, in which it is soluble (Blumberg, *Ph.* [3] 9, 23). Its alkaline salts are soluble.

FUSEL OIL. A volatile liquid present in the product of the alcoholic fermentation of the saccharine liquids derived from potatoes, wheat,

&c., and of the juice of grapes, beet, &c. It passes over in the latter portion of the distillate when these liquids are rectified. Fusel oil always contains amyl and ethyl alcohols, usually isobutyl and *n*-propyl alcohols, some fatty acids, and some ethers.

Fusel oil from potatoes consists chiefly of isoamyl alcohol (*q. v.*); it often contains isobutyl alcohol and decoic acid (Dumas, *A.* 13, 80; Wurtz, *C. R.* 35, 310; *A.* 85, 197; Johnson, *J. pr.* 67, 262). Reibstein (*C. R.* 87, 501) found the following compounds in a litre of potato fusel oil: 275 c.c. isoamyl alcohol; 170 c.c. of products boiling above 132° and still containing amyl alcohol; 150 c.c. isopropyl alcohol; 125 c.c. water; 75 c.c. of a mixture of aldehyde, ethyl alcohol, and ethyl acetate; 65 c.c. *n*-butyl alcohol; 60 c.c. *sec*-amyl alcohol; 50 c.c. isobutyl alcohol; and 30 c.c. *n*-propyl alcohol.

Fusel oil from *molasses* contains isoamyl and isobutyl alcohols (Wurtz, *A.* 93, 107), together with palmitic (?) and heptoic acids and heptoic ether (Mulder, *J.* 1858, 302). Rowney (*C. J.* 4, 372) found isoamyl decoate as well as isoamyl alcohol, water, and EtOH in the fusel oil from the Scotch whisky distilleries.

In fusel oil obtained in preparing alcohol, partly from *wheat*, partly from *maize*, Wetherill (*Chem. Gaz.* 1853, 281) found acetic and octoic acids, isoamyl alcohol, but no butyl alcohol.

In the fusel oil from *beet-root molasses* Fehling (*J. Ph.* [3] 25, 74) found octoic and decoic acids and an ether of decoic acid. In a fusel oil from the same source Perrot (*C. R.* 45, 309; *A.* 105, 64) found ethyl, butyl, and isoamyl alcohols, compound ethers of the above alcohols with caproic, heptoic, octoic, and ennoic acids (*cf.* Müller, *J. pr.* 56, 103). Schrötter (*B.* 12, 1431) found in this fusel oil a liquid base $C_8H_{12}O_2$ (180°–230°) which forms a crystalline sulphate $B'H_2SO_4$. He also observed another base $C_{10}H_{16}N_2$.

FUSIBLE METAL. An alloy of Bi, Pb, and Sn, which melts at 93·7° (*v.* vol. i. p. 511).

FUSTIC. Two yellow dyes are known by this name, viz. *old fustic* obtained from *Morus tinctoria* and *young fustic* from *Rhus calamus.* The latter contains a glucoside 'fustin' $C_{58}H_{46}O_{23}$? crystallising from water in needles [219°], and split up by dilute H_2SO_4 into a sugar and FISETIN (*q. v.*) (Schmid, *B.* 19, 1735).

G

GALACTIN. This name was given by Morin to a nitrogenous body resembling gelatin, said to occur in milk, blood, &c. (*J. Ph.* [3] 25, 423; [4] 14, 11). Wynter Blyth (*C. J.* 35, 531), after freeing milk from casein and albumen, and adding mercuric nitrate, obtained a pp. whence, after removal of mercury as sulphide, and ppg. a second time by lead acetate, a compound $(PbO)_{23}C_{54}H_{78}N_4O_{45}$? was formed. After removing the lead an amorphous alkaloid was left, called by Blyth galactin. More recently the same name has been given by Muntz (*C. R.* 94, 453; *A. Ch.* [5] 26, 121; *Bl.* [2] 37, 409) to a non-nitrogenous carbohydrate $C_6H_{10}O_5$ occurring in the seeds of leguminous plants. Muntz obtained it by exhausting powdered lucerne seeds, *Medicago sativa*, with water containing a little $Pb(OAc)_2$; ppg. excess of lead by oxalic acid; diluting with alcohol (1½ vols.) and purifying the pp. by redissolving in water and reppg. with alcohol. When dried in the air it forms transparent nodules, which swell up in water and dissolve slowly like gum arabic, forming a sticky solution which is ppd. by basic, but not by normal, lead acetate, and behaves generally towards metallic salts like a solution of gum arabic. It is dextrorotatory, $[a]_D = 84{\cdot}6°$. HNO_3 oxidises it to mucic acid. Very dilute mineral acids at 100° give galactose and a non-crystalline sugar. Galactin is not inverted by saliva or pancreatic juice. A substance resembling this galactin occurs in agar-agar (Bauer, *J. pr.* [2] 30, 381).

Paragalactin. This name is given by Schulze a. Steiger (*B.* 20, 290) to the (impure) substance left after exhausting finely-powdered lupin seeds (*Lupinus luteus*) by ether, followed by very dilute cold potash. It constitutes 25 p.c. of the seed, is somewhat gelatinous, and is converted into galactose by boiling dilute acids. After treatment with hot 10 p.c. aqueous KOH alcohol gives a gelatinous pp. whence an acetyl derivative $C_6H_7Ac_3O_5$ can be obtained.

GALACTONIC ACID $C_6H_{12}O_7$. *Lactonic acid.* Small colourless deliquescent needles.

Formation. — By oxidation of milk-sugar (Barth a. Hlasiwetz, *A.* 122, 96; 158, 259), arabinose, or galactose (Kiliani, *B.* 13, 2307; 14, 651, 2529; 18, 1552) with bromine.

Preparation.—A solution of 100 grms. of milk-sugar in 400 c.c. of 5 p.c. sulphuric acid is boiled for 4 hours and freed from H_2SO_4 by $Ba(OH)_2$. The filtrate concentrated to 300 c.c. and cooled to about 35° is oxidised by treatment with 200 grms. of bromine; the yield is 70 p.c. of the theoretical.

Reactions.—By heating to 100° it is converted into its lactone $C_6H_{10}O_6$ by loss of H_2O. It is reduced by HI to the lactone of γ-oxy-*n*-hexoic acid. HNO_3 oxidises it to mucic acid. Potash-fusion gives oxalic and acetic acid. Galactonic acid is slightly lævorotatory. It does not reduce Fehling's solution.

Salts.—A'Na 2aq.—$A'(NH_4)$.—A'_2Ca 5aq.—A'_2Cd aq: monoclinic needles (B. a. H.).—A'_2Cd 4aq.

GALACTOSE *v.* SUGARS.

GALANGIN $C_{15}H_{10}O_5$. [215°]. Occurs, together with camphoride and alpinin, in the galanga-root (Jahns, *B.* 14, 2807). Sublimes in part. Light-yellow tables or flat prisms (containing $\frac{1}{2}C_2H_5OH$); needles (containing H_2O). Sol. ether; S. (90 p.c. alcohol) 1·5; nearly insol. water. Dissolves in alkalis forming a yellow solution. Reduces alkaline silver and copper solutions. On oxidation with HNO_3 it gives benzoic and oxalic acids. — $C_{15}H_8O_5Pb$: amorphous orange pp.

Tri-acetyl derivative $C_{15}H_7O_2(OAc)_3$: [142°]; colourless needles. Sol. alcohol, insol. water.

Di-bromo- derivative $C_{15}H_8Br_2O_5$. Yellow needles.

GALBANUM. A gum resin supposed to be the produce of *Babon Galbanum* or *Ferula erubescens*, and imported from Africa and Persia. Yellowish mass with bitter taste and strong smell. It gives a yellowish-red or violet colour with hydrochloric acid, and an orange colour with a solution of bleaching powder (Hirschsohn, *C. C.* 1877, 182). Yields on distillation with water a small quantity (7 p.c.) of terpene, S.G. $\frac{0}{}$ ·814, (160°), $[\alpha] = -·18$ (Mössmer, *A.* 119, 257). According to Wallach (*A.* 238, 81) oil of galbanum contains a sesquiterpene $C_{15}H_{24}$ whose hydrochloride $C_{15}H_{24}H_2Cl_2$ melts at 118°. Potash-fusion forms resorcin. Contains about 66 p.c. resin, sol. alcohol, ether, and ligroïn, and 25 p.c. gum, sol. water. The resin contains 72 to 74 p.c. carbon, and 8 to 8·5 p.c. hydrogen, and is sol. lime-water. Alcoholic HCl acting on the resin at 100° forms umbelliferon; this body is also formed by the dry distillation of galbanum and other resins formed by umbelliferous plants (Sommer, *Ar. Ph.* [2] 98, 1). The oily distillate from galbanum, when freed from umbelliferon by dilute KOHAq, has a splendid blue colour (289°); it is sol. alcohol, insol. aqueous alkalis, coloured green by alcoholic $FeCl_3$, resinified by Br, and coloured yellowish-red by HNO_3. This blue oil appears to be identical with oil of chamomile (*q. v.*) (Kachler, *B.* 4, 36).

GALIPEINE $C_{20}H_{21}NO_3$. [116°]. An alkaloid present in the Angustura bark. On evaporation of the mother liquor from the oxalate or sulphate of cusparine the salts of galipeine separate out. White prisms, soluble in petroleum, ether, and alcohol. Its salts are more soluble than those of cusparine; their solutions are of a greenish-yellow colour resembling uranium salts. — $B'_2H_2SO_4$ 7aq : [50°]; greenish-yellow prisms.—**Hydrochloride**: prisms with triangular base.—$B'_2H_2PtCl_6$: bright yellow pp. (Körner a. Böhringer, *G.* 13, 365).

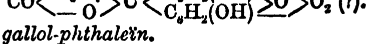
GALITANNIC ACID $C_7H_8O_5$ $\frac{1}{2}$aq. A variety of tannin said to occur in *Galium verum* and *G. Aparine* (Schwarz, *A.* 83, 57).

GALLACETONINE *v.* Pyrogallol.

GALLACETOPHENONE *v.* Tri-oxy-aceto-phenone.

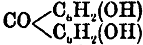
GALLACTIC ACID $C_{14}H_{10}O_9$? Formed by boiling milk-sugar (200 g.) with cupric sulphate (1,200 g.) and NaOHAq (Bœdeker a. Struckmann, *A.* 100, 267). Yellow syrup, miscible with water and alcohol, insol. ether. Ppd. by lime-water and by $Pb(OAc)_2$.—Ca_4A^{iv} 3aq : flocculent pp. — Hg_2A^{iv} 3aq : amorphous pp.—Pb_2A^{iv} 6aq : powder.

GALLEÏN $C_{20}H_{10}O_7$ *i.e.*


$\mathrm{CO}<\genfrac{}{}{0pt}{}{C_6H_4}{—O}>\mathrm{C}<\genfrac{}{}{0pt}{}{C_6H_2(OH)}{C_6H_2(OH)}\geq O>O_2$ (?). *Pyrogallol-phthaleïn.*

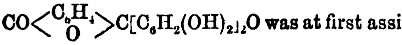
Preparation.—By heating phthalic anhydride (1 pt.) with pyrogallol (2 pts.) at 190°-200°; the fused mass is dissolved in alcohol, filtered, and water added to ppt. the gallein; it is best purified by means of the acetyl-derivative (Baeyer, *B.* 4, 457, 555, 663; Buchka, *A.* 209, 249).

Properties.—Brownish-red powder or glistening, minute crystals with green reflex; sl. sol. hot, insol. cold, water, sol. alcohol, sl. sol. ether, insol. benzene. It dissolves in conc. sulphuric acid with dark-red colouration. Its solution in NH_3Aq and in lime- and baryta-water is violet. Dyes fabrics mordanted with iron or alumina a bluer shade than logwood.

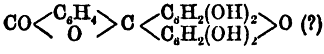
Reactions.—1. With *alkalis* it forms salts, which separate in metallic glistening green crystals; with excess of alkali a blue or blue-violet colouration is produced; but acids reppt. unaltered galleïn from this solution.—2. On reduction with *potash* and *zinc-dust* it yields at first hydrogallein, and then gallin.—3. On reduction in *acid solution* gallol $C_{20}H_{12}O_7$ is formed.—4. Fused with *potash* anhydro-pyrogallolketone 
$\mathrm{CO}<\genfrac{}{}{0pt}{}{C_6H_2(OH)_2}{C_6H_2(OH)_2}>O$ is produced.—5. With *concentrated sulphuric acid* at 190° it yields cœrulein (*q.v.*).—6. HNO_3 oxidises it to phthalic acid.

Tetra-chloro-galleïn $C_{20}H_6Cl_4O_7$ 2aq (at 100°). Formed by heating tetra-chloro-phthalic anhydride with pyrogallol at 195° (Graebe, *A.* 238, 337). Violet powder.

Di-bromo-gallein $C_{20}H_8Br_2O_7$. Formed by adding Br to a solution of galleïn in HOAc. Golden crystals with metallic lustre, v. sol. alcohol, sl. sol. benzene. Its solution in NaOHAq is brilliant blue.

Constitution of Galleïn. The formula 
$\mathrm{CO}<\genfrac{}{}{0pt}{}{C_6H_4}{O}>\mathrm{C}[C_6H_2(OH)_2]_2O$ was at first assigned to galleïn from its analogy in its method of preparation to phenol-phthaleïn, and the formation of a tetracetyl derivative. But its behaviour with reducing agents is not thus explained; in contact with potash and zinc-dust it takes up two atoms of hydrogen, and the product should, were the above formula correct, be analogous to phenol-phthalin and possess acid properties. But the hydrogalleïn shows no acid properties, though on further reduction it yields an acid substance, converted by sulphuric acid into cœrulin, the analogue of phenol-phthalidin. Galleïn is thus possibly a peroxide, a view confirmed by the fact that the tetracetyl derivatives of galleïn and hydrogalleïn are identical (Buchka, *A.* 209, 249).

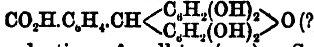
Hydrogalleïn $C_{20}H_{12}O_7$ *i.e.*


$\mathrm{CO}<\genfrac{}{}{0pt}{}{C_6H_4}{O}>\mathrm{C}<\genfrac{}{}{0pt}{}{C_6H_2(OH)_2}{C_6H_2(OH)_2}>O$ (?). Formed by reduction of galleïn (*v. supra*). Crystalline powder, sol. alcohol and HOAc, sl. sol. water, insol. benzene. It dissolves in alkalis with blue colouration; the solution becomes red through oxidation if boiled for a long time.

Tetra-acetyl derivative $C_{20}H_8Ac_4O_7$. [248°]. Formed by boiling hydrogalleïn with Ac_2O, or by heating galleïn with NaOAc and Ac_2O. Small rhombohedra (from benzene); sol. alcohol and HOAc, insol. ether. Gives with Br in HOAc a di-bromo- derivative $C_{20}H_6Br_2Ac_4O_7$. [234°].

Tetra-benzoyl derivative $C_{20}H_8Bz_4O_7$. [231°]. Formed by boiling galleïn with BzCl. Slender needles (from acetone); sol. alcohol and benzene.

Gallin $C_{20}H_{14}O_7$ *i.e.*



$CO_2H.C_6H_4.CH\langle\begin{matrix}C_6H_2(OH)_2\\C_6H_2(OH)_2\end{matrix}\rangle O$ (?). Formed by reduction of gallein (*q.v.*). Small colourless needles, turning red on exposure, sol. alcohol and acetone, sl. sol. water. Decomposes carbonates; converted by conc. sulphuric acid into cœruleïn.

Tetra-acetyl derivative $C_{20}H_{10}Ac_4O_7$: [220°]; colourless leaflets (Buchka, *A.* 209, 268).

Galleïn and gallin dye mordanted fabrics like barwood and logwood.

GALLIC ACID $C_7H_6O_5$ *i.e.* $C_6H_2(OH)_3(CO_2H)$ [5:4:3:1]. Mol. w. 170. [220°–240°]. S. 1 (in the cold); 33 at 100°; S. (ether) 2·5 at 15°; S. (alcohol) 28 at 15°. S.G. $\frac{4}{4}$ 1·694 (Schröder).

Occurrence.—In gall-nuts, in sumach, in hellebore root, in dividivi, in the acorns of *Quercus Ægilops*, in green and black tea, in leaves of *Arctostaphylos uva-ursi*, in sandalwood, in colchicum, in strychnos bark, walnuts, and in most astringent parts of plants (Scheele; Stenhouse, *A.* 45, 9; Kawalier, *Sitz. W.* 9, 290; Hlasiwetz a. Malin, *Z.* 1867, 271; Phipson, *C. N.* 20, 116; Bolley a. Bähr, *Z.* [2] 4, 501).

Formation.—1. By exposing powdered gall-nuts to the air for a month at 20° to 25°; the powder, which must be kept moist, becomes covered with mould, which must be constantly removed, and the product, as soon as the aqueous extract ceases to ppt. a solution of gelatin, is exhausted with water (Scheele; Steer, *Sitz. W.* 22, 249; Wittstein, *Ph.* 12, 444; *cf.* Tieghem, *C. R.* 65, 1091; Weber, *Ph.* [3] 10, 754).—2. A solution of tannin is ppd. by conc. H_2SO_4 and the pp. added to boiling dilute H_2SO_4; after a few minutes gallic acid is deposited in crystals (Liebig).—3. By the action of hot conc. KOHAq on di-iodo-salicylic acid; a considerable portion of the gallic acid being, however, converted into pyrogallol (Lautemann, *A.* 120, 317). Demole (*B.* 7, 1441) could not obtain gallic acid in this way.—4. By the action of aqueous KOH on bromo-veratric acid (Matsmoto, *B.* 11, 139). The acid so prepared melted at 197°-200°.—5. By *potash-fusion* from di-iodo-*p*-oxy-benzoic, bromo-protocatechuic, and bromo-*s*-di-oxy-benzoic acids (Barth a. Senhofer, *B.* 8, 754, 1477; *A.* 142, 247; 164, 118).—6. By heating gum kino with conc. HClAq at 120 (Etti, *B.* 11, 1882).

Separation from tannin.—An infusion of a plant which contains tannin and gallic acid is ppd. by gelatin; the filtrate is evaporated to dryness and exhausted with alcohol; the alcoholic extract is evaporated and the residue crystallised from water, being, if necessary, treated with animal charcoal.

Properties.—Long silky needles or triclinic prisms (containing aq). Astringent taste but no smell. Its solution is strongly acid. At 100°-120° it gives off its water of crystallisation; at 215° it begins to decompose into CO_2 and pyrogallol; but if rapidly heated to 250° there is formed, instead of pyrogallol, a black lustrous insoluble mass, soluble in alkalis (so-called 'Metagallic acid'). An aqueous solution of gallic acid does not change if excluded from the air, but in the presence of oxygen CO_2 is evolved and a black substance is deposited. This decomposition is hastened by the presence of alkalis. Boiling with excess of KOH gives a black substance, the so-called 'tauromelanic acid.' Dilute alcoholic KOH gives 'galloflavin.' A solution of ammonium picrate gives a red colour changing to a beautiful green (Dudley, *Am.* 2, 48). Gallic acid reduces Fehling's solution and ammoniacal $AgNO_3$. Ferric chloride gives a bluish-black pp. (Chevreul, *P.* 17, 176); the pp. dissolves in excess of $FeCl_3$ giving a green solution (Wackenroder, *A.* 31, 78; Etti, *B.* 11, 1882); on heating CO_2 is evolved, the liquid becomes colourless and contains ferrous salt. Pure ferrous sulphate gives no colour at first, but the liquid presently becomes blue. With a mixture of $FeCl_3$ and K_3FeCy_6 gallic acid, like other reducing agents, ppts. Prussian blue. Pure gallic acid does not ppt. gelatin nor alkalis; but when mixed with gum it gives a pp. with gelatin. It gives no pps. with albumen, gelatinised starch or alkaloids, but tartar emetic and NH_4Cl give a heavy white pp. (Meissner, *Ph.* 1889, 626). A solution of gallic acid containing $CaCO_3$ dissolved in CO_2 becomes blue when exposed to the air. A solution of barium gallate gives with excess of $AgNO_3$ a black pp. of silver, and the filtrate contains an acid resembling quercitannic acid (Löwe, *J. pr.* 102, 111; Barfoed, *J. pr.* 102, 314). If a solution of barium gallate BaA'_2 be treated with excess of baryta-water a white pp. is formed which quickly turns blue in contact with the air; but if the ppn. and washing be done with de-aërated water in an atmosphere of hydrogen, the pp. quickly dried *in vacuo* exhibits the composition $BaC_7H_2O_5$ 5aq (Hlasiwetz, *J. pr.* 101, 113). An aqueous or alcoholic solution of gallic acid, containing Na_2SO_4, is coloured by iodine a transient purple-red (Nasse, *B.* 17, 1166). KCy colours an aqueous solution of gallic acid red (difference from tannin); the colour disappears on standing but reappears again on shaking with air (Young, *Fr.* 23, 227).

Reactions.—1. The crystallised acid is unacted on by cold acetic anhydride and even at 100° 2 g. require 2 hours for complete solution. The anhydrous acid behaves similarly towards cold anhydride, but the same quantity only requires $\frac{3}{4}$-hour for solution at 100°. The products are in the first case almost entirely the triacetyl derivative of gallic acid, whereas in the second case there is formed in addition to this a body [151°] having the properties of the pentacetyl derivative of tannin (Böttinger, *A.* 246, 125).—2. Aqueous $KMnO_4$ is quickly decolourised by gallic acid, so that it may be estimated volumetrically in the same way as oxalic acid (Morin, *C. R.* 46, 577). When rubbed with dry $KMnO_4$ it even takes fire (Böttger, *P. Jubelband*, 156). Dilute H_2SO_4 and $KMnO_4$ in the cold give $C_{14}H_{10}O_8$ 'hydrorufigallic acid' a golden crystalline compound which gives a crimson colour with the alkalis and their carbonates (Oser a. Kalmann, *M.* 2, 50).—3. Completely *oxidised* to CO and CO_2 by electrolytic oxygen (Bourgoin, *J. Ph.* [4] 13, 376). *Chromic acid mixture* acts in like manner (Remsen, *Am. S.* [3] 5, 354).—4. An aqueous solution of $KClO_3$ and HCl gives iso-trichloro-glyceric acid $C_3H_3Cl_3O_4$ (Schreder, *A.* 177, 282). If the mother-liquor from which the iso-trichloro-glyceric acid has crystallised be boiled with tin and HCl, the tin ppd. by H_2S, and the liquid extracted by ether, prisms of $C_3H_4Cl_2O_4$ are got.

It forms the salts: $CaH_2A''_2$: minute needles; $BaA''aq$; and $BaH_2A''_2 1\frac{1}{2}aq$.—5. By heating with *bromine* at 100° it is converted into tri-bromo-pyrogallol (Stenhouse, *A.* 177, 189).—6. *Soda-fusion* gives pyrogallol, hexa-oxy-diphenyl, and some phloroglucin (Barth a. Schreder, *B.* 12, 1259; *M.* 3, 649).—7. Hot H_2SO_4 converts it into rufigallic acid $C_{14}H_8O_8$ (*v.* HEXA-OXY-ANTHRAQUINONE).—8. $K_2S_2O_7$ acting upon a solution of gallic acid in concentrated aqueous KOH forms $C_6H_2(OH)_2(O.SO_2.OK)(CO_2K)$ which crystallises in slender needles (Baumann, *B.* 11, 1916). A mixture of gallic and benzoic acids is converted by H_2SO_4 into anthragallol $C_{14}H_8O_5$ (Seuberlich, *B.* 10, 38), *v.* TRI-OXY-ANTHRAQUINONE.—9. Gallic acid is converted by warming with phosphorus oxychloride for some hours into digallic acid $C_6H_2(OH)_3.CO.O.C_6H_2(OH)_2CO_2H$ which is probably identical with tannin (Schiff, *A.* 170, 49).—10. Gallic acid (12 pts.) is converted by heating with *cinnamic acid* (10 pts.) and H_2SO_4 (150 pts.) at 50° into styrogallol $C_{16}H_{10}O_5$ (E. Jacobsen a. Julius, *B.* 20, 2588).—11. By heating with *ammonium carbonate* in a sealed tube an acid $C_8H_6O_7$ is formed.—12. *Formic aldehyde* forms $C_{16}H_{12}O_{10}$ and $C_{16}H_{14}O_{11}$ (Baeyer, *B.* 5, 1096).—13. By heating with *arsenic acid* to 120° ellagic acid $C_{14}H_6O_8$ is formed (Löwe, *Z.* [2] 4, 603). If the product insoluble in water and consisting chiefly of ellagic acid be treated with sodium-amalgam, acidified, and shaken with ether, several substances are extracted, viz.: two crystalline substances $C_{14}H_{10}O_7$ and $C_{12}H_{10}O_8$, both sl. sol. water, and a more soluble crystalline body (Rembold, *A.* 156, 116).

Salts.—$NH_4A'aq$: slender needles (from water). Obtained by passing NH_3 into an alcoholic solution of gallic acid.—$K_2HA'_3aq$: prepared by adding an alcoholic solution of KOH gradually to an alcoholic solution of gallic acid until the pp. begins to be permanent; the liquid is then shaken, when a flaky pp. separates. The pp. is washed with alcohol, dissolved in water, concentrated, and ppd. by alcohol in colourless needles (Büchner, *A.* 53, 187).—$NaA' 3aq$: slender needles; prepared as the K salt.—$BaA'_2 3aq$: prepared by neutralising a boiling solution of gallic acid with $BaCO_3$, filtering, and rapidly concentrating. Small plates; sl. sol. water, insol. alcohol.—$Ba_2C_7H_2O_5 5aq$: *v. supra.*—$SrA'_2 4aq$: small needles; prepared like the Ba salts; sl. sol. water, insol. alcohol.—$CaA'_2 2aq$: crusts of adherent needles; prepared like the Ba salt.—$MgC_7H_4O_5 2aq$: obtained by boiling magnesium acetate with excess of gallic acid, evaporating to dryness, and treating with alcohol to remove free gallic acid. Light white powder; sl. sol. water.—$Mg_3(C_7H_3O_5)_2 6aq$.—$Al_1(C_7H_2O_5)_3 4aq$? Flocculent pp. S. 2·02 at 20°; ·84 at 100° (Lidoff, *J. R.* 1882, 195; *C. J.* 42, 849).—$ZnC_7H_4O_5ZnO$; deposited as a bulky white pp. when gallic acid is added to a solution of zinc acetate.—$CoC_7H_4O_5 3aq$: crimson powder.—$MnC_7H_4O_5 aq$: crystalline powder, turns brown in air.—$PbC_7H_4O_5 \frac{1}{2}aq$; obtained as a white pp. which becomes crystalline by adding lead acetate to an excess of a boiling solution of gallic acid (Liebig, *A.* 26, 128).—$Pb_3(C_7H_3O_5)_2PbO$: yellow crystalline salt; formed by boiling the preceding pp. in its mother liquor.—$SnC_7H_4O_5SnO$: white crystalline powder, obtained by adding gallic acid to a solution of $SnCl_4$ previously neutralised by NH_3.

Acetyl derivative $C_6H_2(OAc)_3.CO_2H$. [166°]. Formed by boiling gallic acid with AcCl or Ac_2O (Nachbaur, *J. pr.* 72, 431; Schiff, *A.* 163, 209; Böttinger, *A.* 246, 125). Prisms (from water); sl. sol. hot water, v. sol. alcohol and ether. Gives no colour with $FeCl_3$.

Bromo-acetyl derivative $C_6H_2(OH)_2(O.C_2H_2BrO).CO_2H$. From gallic acid and bromo-acetyl bromide (Priwoznik, *B.* 3, 644). Amorphous.

Benzoyl derivative $C_6H_2(OBz)_3CO_2H$. Amorphous; softens at 85° (Schiff).

Methyl ether $C_6H_2(OH)_3.CO_2Me$. [192°]. V. sol. water and alcohol (Will, *B.* 21, 2020).

Tri-methyl derivative $C_6H_2(OMe)_3.CO_2H$. [167°]. Needles (from ether or water) (W.).

Methyl ether of the trimethyl derivative $C_6H_2(OMe)_3.CO_2Me$. [81°]. (275°). (W.).

Ethyl ether $C_6H_2(OH)_3.CO_2Et$. [141°] (Etti, *B.* 11, 1882); [150°] (E. a. Z.); [158°] (G.). Formed by passing HCl into a solution of gallic acid (1 pt.) in alcohol (4 pts. of 80 p.c.), evaporating at 70° until the liquid gets thick, adding $BaCO_3$, and extracting the solid mass with ether (Grimaux, *Bl.* [2] 2, 94; Schiff, *A.* 163, 217). Prisms (containing $2\frac{1}{2}$ aq) or anhydrous crystals (from chloroform) (Ernst a. Zwenger, *A.* 159, 28). [90°] when hydrated; [140°–158°] when anhydrous. Sl. sol. cold, v. sol. hot, water; v. sol. alcohol and ether; v. sl. sol. $CHCl_3$. Gives a blue pp. with $FeCl_3$. Reduces ammoniacal $AgNO_3$ and $AuCl_3$. Split up by dry distillation into alcohol, CO_2, and pyrogallol. An aqueous solution saturated by $NaHCO_3$ gives small crystals of $C_7H_4NaEtO_5,C_7H_5EtO_5$. Sl. sol. cold water; on heating with water sodium ellagate $C_{14}H_5NaO_8$ separates. Gallic ether gives a pp. with aqueous $Pb(OAc)_2$, which when dried at 100° has the composition $Pb_3(C_7H_2EtO_5)_2$.

Tri-acetyl derivative of the ethyl ether $C_6H_2(OAc)_3CO_2Et$. Oil, slowly becoming crystalline. Forms no pp. with lead salts.

Isoamyl ether $C_6H_2(OH)_3.CO_2C_5H_{11}$. [139°]. Slender glittering needles; sl. sol. cold water, v. sol. alcohol and ether.

Tri-ethyl-gallic acid $C_6H_2(OEt)_3.CO_2H$. [112°]. Colourless crystals. Sol. hot, sl. sol. cold, alcohol. Formed by boiling its ethyl-ether with alcoholic KOH. **Salts.**—$A'Ag$: [c. 200°]; crystalline solid; sl. sol. cold water.—A'_2Ba: very soluble crystals. *Ethyl ether* $C_6H_2(OEt)_3CO_2Et$: [51°]; glistening needles; v. sol. alcohol, ether, and benzene. Formed by heating the ethyl-ether of gallic acid with ethyl iodide and alcoholic KOH (Will a. Albrecht, *B.* 17, 2099).

Amide $C_6H_2(OH)_3CONH_2$. [243°]. Formed by the action of ammonia and ammonium sulphite on a moderately concentrated alcoholic solution of tannin, the crude product being fractionally crystallised from hydrochloric acid (A. a. W. Knop, *J. pr.* 56, 329; H. Schiff a. Pons, *G.* 15, 177; *B.* 18, 487). Large plates (containing $1\frac{1}{2}$ aq); sl. sol. cold water. Completely decomposed at 245°. Does not combine with HCl. Decomposed by boiling with acids or alkalis into gallic acid and NH_3. The lead compound is a heavy white powder, the copper compound

$C_6H_2(OH)(O_2Cu).CONH_2$

is an azure-blue powder. The acetyl derivative $C_6H_2(OAc)_3.CONH_2$ forms aggregates of colourless crystals, [c. 150°] sol. water, alcohol, HOAc, and benzene.

Bromo-gallic acid $C_6HBr(OH)_3CO_2H$. [above 200°]. Formed, together with the di-bromo- acid, by rubbing gallic acid with bromine (Grimaux, *Bl.* [2] 7, 479; Hlasiwetz, *A.* 142, 250). Monoclinic plates or needles (from water); sl. sol. cold water. Coloured by lime or baryta-water successively red, greenish, and orange. $FeCl_3$ colours it blue-black; alkalis give an orange-yellow colour.

Di-bromo-gallic acid $C_6Br_2(OH)_3CO_2H$. [140°] (G.); [150°] (Etti). Formed as above, using excess of Br. Long brittle needles or plates (containing aq at 100°). Sl. sol. cold water; coloured successively rose, light green, and dark red by lime or baryta-water. Its ethereal solution is turned indigo-blue by baryta-water. Alkalis form an orange solution, turned rose-red on dilution. $FeCl_3$ gives a blue-black solution. With Ag_2O it gives CO_2 and pyrogallol (Priwoznik, *B.* 3, 644). AcCl gives a tetra (? tri-) acetyl derivative crystallising in needles [91°] (P.).

GALLIN *v.* GALLEÏN.

GALLISIN $C_{12}H_{24}O_{10}$ $[\alpha]_J = 77 \cdot 3 – 82 \cdot 7$. The cupric reducing power of 10·98 grams = that of 5 grams of glucose. Occurs in commercial glucose (starch sugar), from the unfermentable residue of which it is obtained by evaporating to a syrup and repeatedly treating with absolute alcohol, and finally with a mixture of alcohol and ether, till all the water has been removed, leaving the substance as a fine powder. White amorphous powder. Very deliquescent. Not fermentable by yeast. Slightly sweet insipid taste. It is insoluble in ether, very slightly in absolute alcohol, more easily in methyl alcohol and acetic acid. It gives no pps. with $Pb(OAc)_2$, $HgCl_2$, Fe_2Cl_6, or $BaCl_2$. It reduces $AgNO_3$ and Fehling's solution. By heating with acids it is converted into glucose.

Salts.—$C_{21}H_{22}BaO_{10}$ 3aq: white pp. formed by adding baryta to gallisin in aqueous alcoholic solution.—$C_{12}H_{23}KO_{10}$: hygroscopic powder.—$C_{12}H_{22}PbO_{10}PbO$: easily soluble white powder.

Hexa-acetyl derivative $C_{12}H_{18}O_4(OAc)_6$: colourless glassy mass, insol. water, e. sol. alcohol, ether, benzene, CS_2, &c. (Schmitt a. Cobenzl, *B.* 17, 1000, 2456).

GALLIUM Ga. At. w. 69·9. Mol. w. unknown as V.D. of element has not been determined. [30·15°]. S.G. $\frac{24 \cdot 5^\circ}{24 \cdot 5^\circ}$ 5·96 solid; 6·07 liquid. S.H. ·079 solid; ·0802 liquid. Latent heat of fusion = 1911 gram-units. Melted Ga remains liquid at temperatures considerably under the M.P., but solidifies by contact with a trace of solid Ga; other metals do not cause solidification. The metal crystallises in quadratic octahedra. Characteristic lines in the emission-spectrum are 4170 and 4031; both lines have been reversed by Liveing and Dewar (*Pr.* 28, 471).

Gallium was discovered by Lecocq de Boisbaudran in August 1875 in *zinc-blende* from Pierrefitte (Hautes-Pyrénées); the observation of two violet lines in the spark-spectrum of this blende led to the discovery of the new element. The properties of Ga were found to be those of the element *eka-aluminium* as predicted by Mendelejeff (*v. Chemical relations of Gallium*).

References.—The memoirs of Lecocq de Boisbaudran are contained in *C. R.* 81, 493, 1100; 82, 168, 1036, 1098; 83, 611, 636, 663, 824, 1044; 86, 756, 941, 1240; 93, 294, 329, 816; 94, 695, 1154, 1227, 1439, 1625; 95, 18, 157, 410, 503, 703, 1192, 1332; and with Jungfleisch in *C. R.* 86, 475, 577. There are also memoirs by Berthelot in *C. R.* 86, 786; Dupré, *C. R.* 86, 720, Mendelejeff, *C. R.* 81, 909; Nilson a. Pettersson, *C. R.* 91, 232. A general account of gallium is given by de Boisbaudran in Fremy's *Encyclopédie Chimique*, tome iii. cahier 5, pp. 202 *et seq.* [1884].

Occurrence.—In very small quantities in various zinc-blendes, and in many specimens of commercial zinc. The best source of the metal is the blende from Bensberg on the Rhine; de Boisbaudran and Jungfleisch obtained 52 grams of pure gallium from 4300 kilos. of this blende.

Testing blendes for gallium.—The blende is treated with *aqua regia*, the solution is heated to remove nitric acid; when cold, zinc (free from Ga) is added; various metals are thus ppd.; while H is still being evolved the liquid is poured through a filter; large excess of Zn is added, and the liquid is boiled until a white pp. forms; this pp. is collected, washed, and dissolved in HClAq; the solution is concentrated to a small volume, and examined by causing a small induction-spark to play over the surface of the liquid, and passing the light through a spectroscope. 10 grams of a gallium-containing blende is sufficient to give the chief spectral lines of Ga.

Preparation.—1. The powdered blende is treated with *aqua regia*, excess of blende being always present in order to saturate the nitric acid; to the filtered liquid, when cold, Zn (free from Ga) is added; Sb, As, Bi, Cd, Cu, Au, In, Pb, Hg, Ag, Tl, Sn, and Se if present, are thus ppd.; while H is still coming off, the liquid is filtered; the filtrate is boiled with a large excess of Zn until a white pp. appears; this pp. contains all the Ga as hydrated oxide (or as a basic salt) mixed with Al_2O_3, basic salts of Fe, Zn, Cr, Co, and some SiO_2. The pp. is dissolved in HClAq, and H_2S is passed into the liquid; the pp. is removed by filtration; $NH_4C_2H_3O_2Aq$ or $NaC_2H_3O_2Aq$, and acetic acid are added to the filtrate, which is then ppd. by H_2S; it is advisable to ppt. fractionally and to continue until the filtered liquid ceases to show Ga lines in the spectroscope; if the filtrate from the last batch of pp. shows the lines of Ga, a zinc salt must be added and the process of ppn. repeated. The pp. by H_2S, which contains all the Ga, is well washed and then dissolved in HClAq; the Ga is then ppd. by one of the following methods: (1) the solution is boiled with as small an excess of Zn as suffices to ppt. the Ga; (2) the solution is boiled till H_2S is all off, and then fractionally ppd. by NH_3Aq or NaOHAq; (3) H_2S is removed, and Ga oxide is ppd. by addition of $BaCO_3$ or $CaCO_3$. The crude Ga oxide obtained by one of these methods is washed and dissolved in HClAq; some Na_2SO_3 is added (to reduce $FeCl_3$ to $FeCl_2$), and the liquid is boiled for some time; excess of $CaCO_3$ is then added, and the liquid is filtered at once, as far as possible out of contact with air; this treatment is repeated twice; the greater part of the impurities is thus removed. The ppd. Ga oxide mixed with $CaCO_3$ is dissolved in HClAq; NH_3Aq is added in excess, and the liquid is boiled until it shows an acid reaction, water being added from time to time; the pp. is dissolved in H_2SO_4Aq, and the liquid is evaporated until white fumes come off; the last traces of chlorides are thus removed. To the sulphate is added considerable excess of pure KOH (free from chloride). After gentle warming the liquid is filtered (oxides of Fe and In are thus removed), and the strongly alkaline liquid is electrolysed, Pt electrodes are used, and the positive plate should be 6 to 10 times larger than the negative. The Ga is removed by the finger from the Pt plate under warm water, and allowed to stand for an hour or two in water acidulated with pure HCl, and then in dilute pure potash solution for a little at 50°-60°; it is then washed with water. 2. Iron may be used in place of zinc to effect the reduction of the solution of the blende; only a little Cd, Pb, &c., are thus ppd., so that the first filtration is omitted. The liquid containing Fe is boiled till a white pp. forms, $CaCO_3$ in slight excess is added, and the liquid is filtered at once. The pp. is dissolved in HClAq, and the liquid is reppd. by $CaCO_3$, Na_2SO_3 being added to prevent oxidation of ferrous iron. Finally the pp. is dissolved in HClAq, and oxides of Cr and Al are removed by one of the following methods: (1) tartaric acid and a Mn salt are added, and then excess of NH_3Aq; addition of NH_4 sulphide then ppts. MnS, and with it all the Ga; this treatment is repeated two or three times; the pp. is then dissolved in HClAq, digested when cold with $CaCO_3$, and the ppd. Ga oxide mixed with $CaCO_3$ is heated as directed in 1; (2) K_4FeCy_6 is added to the solution in HCl; the pp. is washed with water containing $\frac{1}{4}$ to $\frac{1}{3}$ its weight conc. HClAq; the ferrocyanide pp. is then dried and fused with $KHSO_4$, and the fused mass is treated with water; to the solution excess of NH_3Aq is added, and it is then boiled for some time; the pp. is washed and dissolved in HClAq, and this liquid is treated with Na_2SO_3 and $CaCO_3$ as directed in 1.

Properties.—A grey metal, with greenish-blue reflection; fairly hard; crystallises in quadratic octahedra; brittle, but may be hammered into thin plates, which can be bent without breaking. When melted, Ga is a silver-white liquid with faint reddish reflection. It melts at 30·15° and remains liquid nearly to 2°; if a small piece of solid Ga is placed in the liquid metal below 30·15° the whole solidifies; metals other than Ga fail to produce solidification. According to J. Regnauld, liquid Ga is electronegative to solid Ga (*C. R.* 86, 1457). Ga is unchanged in air or boiling water. Heated in air to full redness it does not volatilise, and is oxidised only superficially. It is superficially oxidised when heated to redness in dry O. The atomic weight of Ga has been determined (1) by converting a known mass of the metal into oxide (De Boisbaudran, *C. R.* 86, 941); (2) by strongly heating gallium-ammonium alum (De B., *l.c.*); (3) from determinations of the V.D. of $GaCl_3$, $GaCl_2$ (Nilson a. Pettersson, *C. J. Trans.* 1888. 822); (4) by determining S.H. of Ga; (5) by establishing that Ga-NH_4 sulphate is isomorphous with alum, and hence assigning a formula to the Ga compound (*v.* also *Chemical relations of Gallium*). As the chlorides $GaCl_3$ and $GaCl_2$ have both been gasified (Nilson a. Pettersson, *C. J. Trans.* 1888. 822) the atom of Ga appears to be both divalent and trivalent in gaseous molecules.

Reactions.—1. Heated to full redness in *air*, or *oxygen*, Ga is superficially oxidised.—2. Does not decompose *water* at 100°.—3. Dissolved slowly by *hydrochloric acid* with evolution of H. 4. *Warm nitric acid* dissolves Ga, forming nitrate.—5. Slowly dissolved by *potash solution*, also by *ammonia*.—6. Combines rapidly with *chlorine* at ordinary temperature, more slowly with *bromine*, and with *iodine* only when heated. 7. Alloys very easily with *aluminium*; the alloys decompose cold water rapidly.

Separation and Estimation of Gallium; *v.* De Boisbaudran, *C. R.* 93, 816; 94, 1154, 1227, 1439, 1625; 95, 157, 410, 503, 703, 1192, 1332.

Chemical relations of Gallium.—Gallium is the fourth member of Group III., in the grouping of the elements according to the periodic law. When Mendelejeff published his first extensive memoir on the periodic law, he was obliged to leave the positions III.-4 and III.-5 unfilled; none of the known elements could be placed in either of these places. Mendelejeff, however, predicted the properties of the elements which would be discovered to fill the vacancies. One of the two unknown elements was assigned a place in series 5. Now the differences between the values of the atomic weights of the elements in series 3 and 5, beginning with Group I. (and omitting Group III. as the unknown element we are considering is placed in that group) are, 40 in Group I., 41 in Group II., 44 in Group IV., 44 in Group V., 47 in Group VI., and 44·5 in Group VII. Hence, it was argued, the difference will be about 42 in Group III.; but the element in III.-3 is Al with at. w. 27; hence the unknown element in III.-5 will have an at. w. of about 27 + 42 = 69. By tabulating the differences between the atomic weights of elements in series 4 and 5, of course omitting Group III., the following numbers are obtained; 24, 25, —, 24, 24, 27, 25. Hence in Group III. the difference will be about 25; but there was a gap in series 4 Group III., hence it was necessary first of all to calculate a value for the at. w. of the unknown element which ought to find a place in III.-4, and then to add 25 to this value. The result was that the element in III.-4 should have the at. w. 44; hence, 44 + 25 = 69. Having thus determined the at. w. of the element which would be placed in III.-5 when it was discovered, Mendelejeff proceeded to determine the properties of this element by studying (1) the properties of the members of Group III., (2) the properties of the members of series 5, (3) the relations between Group III. as a whole and other groups, especially considering the position of the group in the complete scheme of classification, and (4) the relations of series 5 to other series. Group III. is on the whole composed of metals; the only decided non-metal is B; but B is succeeded by the metal Al. As the unknown element would come next but one to Al, and would be followed by Y, La, In, Yb, Tl, it would certainly be a metal, and would resemble Al generally. Then considering that the unknown element would follow the metals Cu and Zn, in series 5, and would be followed by the element As which is both metallic and non-metallic, As being succeeded by the non-metals Se and Br, it might safely be asserted that the unknown element would be metallic, but probably less metallic than Cu and Zn. The composition and properties of the compounds of the Al group of elements determined the general composition and properties of the compounds of the unknown metal; it would form an oxide M_2O_3, a chloride M_2Cl_6 or MCl_3, it would form salts M_23SO_4, $M3NO_3$, &c. Then, considering the position of the element as regards Al, it was argued that the relations of this body, when discovered, to Al would be somewhat similar to those of Zn to Hg, or As to P, or Se to S. But as Zn is less like Hg than As is like P, and as As is less like P than Se is like S, it was concluded that the resemblance between the new element and Al would be fairly close, although not quite so marked as that between As and P, or Se and S; hence, it would probably form an alum. Guided by such reasoning as this, Mendelejeff was able to tabulate precisely the properties of the element which he placed in III.-5, and to which he gave the name of *eka-aluminium*. The properties of gallium were found to agree extremely closely with those of *eka-aluminium* (*v.* table in vol. i. p. 352).

Lecocq de Boisbaudran calculated the at. w. of Ga by comparing its spectrum with those of analogous elements, and comparing this result with the spectral relations of similar elements, the at. ws. of all of which were known. The at. ws. of the three similar elements K, Rb, Cs, show the following relations:—

	At. w.	Differences	
K . . .	39·1		
		46·26	
Rb . .	85·36		1·38
Cs . .	133	47·64	

The increase in at. w. from Rb to Cs = increase from K to Rb × 1 + ·02983. Then comparing the wave-lengths of the chief pairs of lines in the spectra of these three elements, we get this result:—

	Wave-lengths	Means	Differences	
K . .	5831 5812	5821		
			429	
Rb . .	6297 6203	6250		170
			599	
Cs . .	6975 6723	6849		

The increase in wave-length from Rb to Cs = increase from K to Rb × 1 + ·3963.

Turning now to the three elements of which Ga forms the middle member, we have:—

	At. w.	Differences
Al . . .	27·5	
Ga . . .	?	86·0
In . . .	113·5	

And tabulating the wave-lengths of the principal pairs of lines, we have:—

	Wave-lengths	Means	Differences	
Al . .	3963 3944	3953		
			147	
Ga . .	4170 4031	4100		59
			206	
In . .	4511 4101	4306		

The increase in the wave-length from Ga to In = increase from Al to Ga × 1 + ·4014. Then if it is assumed that the increase in wave-length (λ) is related to the increase in atomic weight (α) similarly in both sets of elements, we have the statement:—

$$\lambda\text{K to Cs} : \alpha\text{K to Cs} = \lambda\text{Al to In} : \alpha\text{Al to In}$$
$$\cdot 3963 : \cdot 02983 = \cdot 4014 : x$$
$$\text{and } x = \cdot 030214.$$

Now, putting the difference of at. w. between Al and Ga as A, the difference between Ga and In as B, we find that B = A(1 + ·030214); and as A × (2 + ·030214) = 86, it follows that A = 42·36, and B = 43·64; hence the at. w. of Ga is found to be (1) 27·5 + 42·36 = 69·86, and (2) 113·5 − 43·64 = 69·86. The observed at. w. is 69·9.

For the properties of the elements of Group III., to which Ga belongs, *v.* EARTHS, METALS OF THE, p. 424.

Gallium bromides. Ga and Br combine directly to form a colourless crystalline mass, which is less volatile than $GaCl_3$. Probably two bromides, $GaBr_2$ and $GaBr_3$, are produced; but they require further investigation.

Gallium chlorides. Two are known, $GaCl_2$ and $GaCl_3$. Both have been gasified.

GALLIUM DICHLORIDE $GaCl_2$. Mol. w. 140·64. V.D. at 1000°–1400° 60·6 (Nilson a. Pettersson, *C. J.* 53, 825). Prepared by heating Ga in Cl, keeping the metal in excess; or better, by heating $GaCl_3$ with Ga for a long time, and then distilling in dry CO_2 (N. a. P., *l.c.*). White transparent crystals, melting at 164°, and boiling at c. 535°. When melted it may be kept for a long time without solidifying. Vapour fumes in the air. Deliquesces in moist air to a clear liquid; addition of water causes ppn. of a grey solid (? oxychloride or suboxide, or GaCl *v.* N. a. P., *l.c.*), and evolution of H. Solution of $GaCl_2$ in HClAq reduces $KMnO_4Aq$. At a white heat $GaCl_2$ appears to decompose into Cl and a lower chloride (N. a. P., *l.c.*).

GALLIUM TRICHLORIDE $GaCl_3$. Mol. w. 176·01. V.D. 440° to c. 1000° 89; at 350° V.D. = 128 (Nilson a. Pettersson, *C. J.* 53, 824). V.D. 237°–307° 161·6; at 377·6° V.D. = 113·2 (Friedel a. Crafts, *C. R.* 107, 306). These results point to the existence of Ga_2Cl_6 at c. 250°, and to the gradual dissociation of this molecule into $GaCl_3$. S.G. $\frac{80^\circ}{80^\circ}$ 2·36.

$GaCl_3$ may be prepared by heating Ga in excess of Cl, and distilling the product in N, or by heating Ga in dry HCl gas free from air. It forms long white needles, which melt at 75·5° and boil at c. 215°–220°. When melted it remains liquid at temperatures below its m.p.

Molten $GaCl_3$ absorbs gases readily, *e.g.* N and Cl, and gives them off again on crystallising. It is deliquescent in moist air; dissolves in water with production of much heat. When this solution is evaporated an amorphous mass is obtained, which absorbs moisture and becomes gelatinous. When this gelatinous substance was kept in closed tubes for several years small crystals were obtained having the composition $Ga_2Cl_6.Ga_2O_3.13H_2O$ (L. de B.). At about 1100° $GaCl_3$ begins to decompose into $GaCl_2$ and Cl (N. a. P., *l.c.*).

Gallium ferrocyanide is ppd. as a white salt by adding K_4FeCy_6Aq to solution of $GaCl_3$. Composition not determined.

Gallium iodides. Two probably exist, corresponding with the two chlorides; but they have not been thoroughly investigated. Ga and I combine when heated together.

Gallium oxides. Two probably exist.

Gallium monoxide (? GaO) is probably formed by heating Ga_2O_3 to redness in a stream of H. The substance thus formed is a greyish-blue mass, which dissolves in HNO_3Aq and in dilute HClAq; the solution in HClAq decolourises $KMnO_4Aq$.

Gallium sesquioxide Ga_2O_3. White solid, formed by heating $Ga3NO_3$. Dissolves in acids to form Ga salts. Does not melt at white heat. Reduced to Ga by H at a high temperature. S.H. ·1062. Hydrated gallium oxide (? GaO_3H_3) is ppd. from solutions of Ga salts by carbonates and bicarbonates of the alkalis. It is sol. in excess of the pptant., more sol. NH_3Aq and $(NH_4)_2CO_3Aq$, and v. sol. KOHAq.

Gallium, salts of. Only a few salts have been prepared. The chief are $Ga3NO_3$ and Ga_23SO_4 (*v.* Nitrates and Sulphates). They are obtained by dissolving Ga_2O_3 in acids and evaporating. The sulphate forms an ammonia-alum $Ga_23SO_4.(NH_4)_2SO_4.24H_2O$.

Sulphydric acid does not ppt. Ga salts. If, however, the solution is alkaline, or is acidified by a weak acid, and a metal is present whose salts are ppd. by H_2S, *e.g.* Zn, then the Ga is also ppd. *Potash* ppts. Ga salts; the pp. is e. sol. in excess of the pptant. *Potassium ferrocyanide* gives a pp. with so little as $\frac{1}{175.000}$ part of a Ga salt in an HCl solution. *Barium carbonate* ppts. Ga_2O_3 in the cold. *Zinc* does not ppt. Ga from acid solutions; but as soon as the acid has been neutralised by the Zn white flocks of Ga_2O_3 ppt.

Gallium sulphide. The white pp. obtained by passing H_2S into a conc. solution of $GaCl_3$ in NH_3Aq, to which NH_4 tartrate has been added, is probably a sulphide of Ga. M. M. P. M.

GALLOCARBOXYLIC ACID *v.* Pyrogallol-di-carboxylic acid.

GALLOCYANINE $C_{15}H_{12}N_2O_5$. Formed by heating gallic acid and the hydrochloride of nitroso-dimethyl-aniline in an alcoholic or HOAc solution (Nietzki a. Otto, *B.* 21, 1740; *cf.* Pabst, *Bl.* [2] 38, 162; Köchlin, *C. N.* 47, 170). Shiny green needles, almost insol. water, alcohol, and HOAc. Sol. alkalis with reddish colour. Conc. acids dissolve it with reddish-violet colour. The salts so formed are decomposed by water. Dyes wool, mordanted with chromium, bluish-violet.

Anilide $C_{27}H_{24}N_4O_4$. Lustrous green needles.

Methyl ether $C_{15}H_{11}N_2O_5Me$. '*Prune.*' Formed by the action of nitroso-dimethyl-aniline hydrochloride on the methyl ether of gallic acid. Is more basic than gallocyanine and forms a crystalline hydrochloride. Dyes cotton, mordanted with tannin, or wool or cotton mordanted with chromium, bluish-violet.

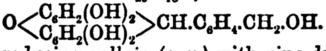
Di-acetyl derivative of the methyl ether $C_{15}H_9N_2O_5MeAc_2$. Small greenish needles (from alcohol).

GALLOFLAVIN $C_{13}H_6O_9$? Obtained by dissolving gallic acid (50 g.) in alcohol (875 c.c.) and water (1000 c.c.), cooling to 0°, adding 135 c.c. of 28 p.c. aqueous KOH, and passing air through the solution (Bohn a. Graebe, *B.* 20, 2327). Greenish-yellow plates, sl. sol. water, alcohol, and ether. Dissolves in alkalis and their carbonates forming yellow solutions. Dyes wool, mordanted with chromium, yellow.— $C_{13}H_4K_2O_9$: greenish-yellow crystals, v. sl. sol. cold water; boiling water liberates free galloflavin.

Acetyl derivative $C_{13}H_2Ac_4O_9$. [230°]. White needles, v. sol. HOAc.

Chloro-acetyl derivative $C_{13}H_2(C_2ClH_3O)_4O_9$. [212°].

GALLOL $C_{20}H_{18}O_7$ *i.e.*



$O\langle{}^{C_6H_2(OH)_2}_{C_6H_2(OH)_2}\rangle CH.C_6H_4.CH_2.OH$. Formed by reducing gallein (*q. v.*) with zinc-dust and dilute H_2SO_4 (Baeyer, *B.* 4, 556; Buchka, *A.* 209, 264). Crystals, changing in the air to a reddish powder. Sl. sol. cold water and ether, v. e. sol. alcohol.

Penta-acetyl derivative $C_{20}H_{13}Ac_5O_7$. [230°].

GAMBOGE. A gum-resin which appears to be produced from *Stalagmites cambogioides*, a tree growing in Siam. It contains about 72 p.c. resin and 20 p.c. gum. Its powder is yellow. It is a drastic purgative. It dissolves in alcohol and ammonia; the ammoniacal solution gives a red pp. with $BaCl_2$, and yellow pps. with $ZnSO_4$, with lead salts, and with $AgNO_3$. Ether extracts a red resin which forms a yellow powder; it decomposes boiling alkaline carbonates forming red salts (Buchner, *A.* 45, 94; Christison, *A.* 76, 344; Costelo, *Ph.* [3] 9, 1022). Potash-fusion gives phloroglucin, acetic acid, isouvitic acid $C_9H_8O_4$, and pyrotartaric acid (Hlasiwetz a. Barth, *A.* 138, 61).

GARDENIN $C_{14}H_{12}O_6$. [164°]. Extracted from 'dekamali,' a resin from *Gardenia lucida.* After removing the volatile oil by distilling with steam, the residue is extracted with weak spirit, from which gardenin crystallises on cooling. It may be purified by successive crystallisation from benzene and petroleum spirit (Stenhouse a. Groves, *C. J.* 31, 551; 35, 689; *cf.* Flückiger, *Ph.* [3] 7, 589). Deep yellow crystals. Almost insol. water, m. sol. alcohol. Insol. alkalis, sol. hot HClAq. Its solution in HOAc (30 pts.) treated with HNO_3 (S.G. 1·45) gives gardenic acid.

Gardenic acid $C_{14}H_{10}O_6$? [c. 223°]. Deep crimson needles, insol. water, light petroleum, CS_2, and almost insol. ether and benzene. Sol. alkalis.

Acetyl derivative $C_{14}H_8Ac_2O_6$. [244°]. Formed by the action of glacial acetic acid. Insol. water, light petroleum, and CS_2. Almost insol. ether and benzene. Sol. alkalis.

Hydrogardenic acid $C_{14}H_{14}O_6$. [190°]. Formed by the action of H_2SO_3 on gardenic acid. Flat needles. May be re-oxidised to gardenic acid.

GARLIC OIL. Contains allyl sulphocyanide (Wertheim, *A.* 51, 289) and a sesquiterpene $C_{15}H_{24}$ (254°) (Beckett a. Wright, *C. J.* 29, 1).

GARRYINE. A substance crystallising in cubes and occurring in the leaves and roots of *Garrya Fremonti.* It is sol. water and alcohol and gives a purple colour with H_2SO_4 (Ross, *Ph.* [3] 8, 489).

GASES, ABSORPTION OF. The more important chemical aspects of the absorption of gases are treated in the article DISSOCIATION; *v.* especially pp. 395-399.

GASES, ANALYSIS OF, *v.* ANALYSIS, vol. i. pp. 232-247.

GASES, COMBINATION OF, BY VOLUME, *v.* COMBINATION, CHEMICAL, LAWS OF, pp. 236, 238.

GASES, DIFFUSION OF, *v.* DIFFUSION, p. 384; and also PHYSICAL METHODS.

GASES, TRANSPIRATION OF. The rate of flow of gases through capillary tubes is generally called the transpiration of gases. Measurements of *transpiration-constants* are more important in physical than in chemical inquiries.

GASIPEÏNE, a misprint for GALIPEÏNE.

GAULTHERIA OIL, or *Oil of Wintergreen,* is obtained from the leaves of *Gaultheria procumbens,* growing in New Jersey, by steam distillation. It consists of methyl salicylate (222°) mixed with a small quantity of a terpene $C_{10}H_{16}$ (160°). V.D. 4·92 (Cahours, *A. Ch.* [3] 10, 327; Procter, *J. Ph.* [3] 3, 275; *A.* 48, 66; Biedermann, *B.* 8, 1677).

GEISSOSPERMINE $C_{19}H_{24}N_2O_2$. [160°]. $[\alpha]_D = -93·4°$ in a 1·5 p.c. solution at 15°. An alkaloid occurring in the Pereira bark (Hesse, *A.* 202, 143; *B.* 10, 2162). Small white prisms (containing aq), sol. dilute acids but reppd. on neutralisation. Sl. sol. ether. Forms a purple solution in conc. HNO_3Aq. It does not reduce H_2PtCl_6 (Wulfsberg, *Ph.* [3] 11, 269). It gives pps. with $HgCl_2$, with $K_2Cr_2O_7$, with potassio-mercuric iodide, and with potassium picrate.

Salts.—$B'_2H_2PtCl_6$: yellow flocculent pp.—Aurochloride: brown amorphous pp.—Oxalate: minute needles.—Sulphate: white needles.

GELATIN *v.* PROTEIDS, *Appendix C.*

GELOSE $C_6H_{10}O_5$. Forms the essential constituent of China moss or Haï-Thao (Payen, *C. R.* 49, 521; Morin, *C. R.* 90, 924). Used for finishing cotton goods (Heilmann, *D. P. J.* 213, 522). When dissolved even in 500 times its weight of water it forms a jelly on cooling. After drying it is insol. cold water, alcohol, ether, weak alkalis or acids, and Schweizer's solution. Dilute HNO_3 oxidises it to mucic acid. Its aqueous solution is ppd. by alcohol. Dilute HCl, acetic acid, and oxalic acid deprive it of its property of gelatinising; heating with water under 6 atmospheres' pressure has a like effect. A 10 p.c. aqueous solution is lævorotatory, $[\alpha] = -4° 15'$; but boiling acidulated water slowly changes this to a nearly equal dextrorotation, the resulting solution reducing Fehling's solution, and being no longer ppd. by alcohol. By treating gelose with water at 100° Porumbaru (*C. R.* 90, 1081) got a lævorotatory sugar $C_6H_{12}O_6aq$.

GELSEMINE $C_{22}H_{38}N_2O_4$. S. (ether) 4. May be extracted by alcohol from the root of *Gelsemium sempervirens* (Wormley, *Ph.* [3] 13, 106; Gerrard, *Ph.* [3] 13, 502, 641; Robbins, *B.* 9, 1182; Thompson, *Ph.* [3] 17, 803). Amorphous solid, melting below 100°. Sl. sol. water, m. sol. alcohol, v. sol. ether and chloroform. Its solution has a bitter taste and is strongly alkaline. It is very poisonous, producing convulsions. Its hydrochloride is ppd. by the usual reagents for alkaloids. Conc. H_2SO_4 gives a greenish-yellow solution soon turning reddish-brown; on adding $K_2Cr_2O_7$ a cherry-red colour turning to bluish-green appears. HNO_3 turns it green.

Salts.—B'HCl: amorphous.—$B'_2H_2PtCl_6$: amorphous. Using the formula $C_{54}H_{69}N_4O_{12}$. Thompson describes the salts $B'H_3Cl_3$, $B'(HAuCl_4)_3$, and $B'_2(H_2PtCl_6)_3$.

Gelseminine. A resinous alkaloid which, according to Thompson, accompanies gelsemine.

Gelsemic acid. An acid which, according to Wormley, occurs in *Gelsemium sempervirens* and may be extracted by ether from the acidulated root. It dissolves in 2,912 pts. of water and in 330 pts. of ether. HNO_3 turns it yellow, the solution becoming deep red on addition of ammonia. Gelsemic acid forms fluorescent solutions and is perhaps identical with æsculin.

TRIGENIC ACID *v.* ETHYLIDENE-BIURET.

GENTIANIN $C_{14}H_{10}O_5$ *i.e.* $C_6H_3(OH)_2.CO.C_6H_2MeO_2$. *Gentisin. Gentianic acid.* The colouring matter of the root of *Gentiana lutea* growing in Switzerland and the Tyrol and used as a tonic (Henry a. Caventou, *J. Ph.* 7, 173; Baumert, *A.* 62, 106; Trommsdorff, *A.* 21, 134; Leconte, *A.* 25, 202; Hlasiwetz a. Habermann, *B.* 7, 652; *A.* 175, 63; 180, 348). Pale-yellow needles, v. sl. sol. water, m. sol. ether, v. sol. boiling alcohol. Neutral to litmus. Alkalis dissolve it, yielding a deep golden solution. Between 300° and 340° it may be partially sublimed, but the greater part is carbonised. It is not attacked by dilute acids. Conc. H_2SO_4 forms a yellow solution. HNO_3 (S.G. 1·43) forms a green solution from which water throws down green $C_{14}H_8(NO_2)_2O_5aq$. Fuming HNO_3 appears to form $C_{14}H_7(NO_2)_3O_5$. Potash-fusion splits up gentianin into phloroglucin, gentisic acid, and acetic acid. Gentianin reduces $AgNO_3$. Sodium-amalgam forms $C_{13}H_{10}O_4$ an amorphous red body.

Salts.—KHA″aq.—$KH_3A''_2$ 2aq.—$K_2H_8A''_5$ 17aq.—NaHA″ 2aq: golden needles.—$Na_2H_4A''_3aq$. — $Na_4H_{10}A''_7$ 2aq. — BaA″aq. — PbA″Pb$(OH)_2$.

Acetyl derivative $C_{14}H_8Ac_2O_5$. [196°]. Slender crystals (from alcohol).

GENTIANOSE $C_{36}H_{66}O_{10}$. [210°]. Prepared from the juice of *Gentiana lutea* (taken in September) by exhausting with alcohol (95 p.c.) and fractionally ppg. with ether (A. Meyer, *H.* 6, 135). Colourless tables with sweet taste. Sol. water. Its aqueous solution is fermented by yeast. It is charred by H_2SO_4. It does not reduce Fehling's solution. It is dextrorotatory.

GENTIOPICRIN $C_{20}H_{30}O_{12}$. [121°-125°]. Occurs in the root of *Gentiana lutea* (Kromayer, *Ar. Ph.* [2] 110, 27). Needles; v. sol. water, sl. sol. alcohol, insol. ether; tastes bitter. Reduces hot ammoniacal $AgNO_3$. Does not reduce Fehling's solution. Split up by dilute acids into amorphous gentiogenin $C_{14}H_{16}O_5$ and a fermentable sugar.

GENTISIC ACID *v.* DI-OXY-BENZOIC ACID.

GENTISIC ALDEHYDE *v.* DI-OXY-BENZOIC ALDEHYDE.

GENTISIN *v.* GENTIANIN.

GEOLOGICAL CHEMISTRY. Since geology is a science which deals primarily with the constitution and history of the earth, it is evident that there must be many points at which it comes into relation, directly or indirectly, with chemistry. Much of geological science is devoted to the study of *rocks*, or those large masses of mineral matter which build up the crust of the earth. The chemist is of service to the geologist not only in analysing these rocks, or the mineral species of which they are composed, but in explaining some of the processes by which the rocks themselves may have been originally formed, and in tracing the nature of the alterations to which they have been subjected since their formation. Hence the geological chemist gives special attention to those natural processes of rock formation in which chemical reactions are involved, and he endeavours to imitate the operations of nature by experiment in the laboratory. The experimental method was first introduced into geology by Sir James Hall, of Dunglass, who, in order to explain the origin of certain crystalline limestones, subjected pounded chalk to a high temperature in closed gun-barrels, and obtained, under certain conditions, a crystalline mass of carbonate of calcium somewhat resembling a saccharoidal marble (*T. E.* 6, 101, 121). It must be remembered, however, that much of the experimental work recorded in the literature of chemical geology refers to the synthesis of minerals rather than of rocks. A rock may, it is true, be composed of only a single mineral, but in most cases a rock is an aggregate of several distinct mineral species, and although the synthesis of each constituent may be successfully effected, it by no means follows that this work will throw light upon the origin of the composite rock. (For an excellent account of the present condition of mineral synthesis, see M. L. Bourgeois, *Reproduction artificielle des minéraux*, in Fremy's *Ency. Ch.* 1884; and Fouqué and Lévy's *Synthèse des Mineraux et des Roches*, Paris, 1882.)

Analysis of Rocks. — The simplest method is of course to analyse the rock as a whole, and in the case of a very fine-grained rock in which it is impossible to separate the mineral constituents individually, this is the only available method. The interpretation of the results of such an analysis requires, however, considerable sagacity, more especially if the constitution of the rock be complex. Two rocks, distinct in composition, such as a granite and a trachyte, may give the same bulk-analysis, while two rocks of similar mineral composition may yield different analyses. When the oxygen ratio, or quantivalent ratio, of a rock is known, as also that of each of its mineral components, it may be possible to calculate the percentage of each mineral in the rock (*v.* S. Haughton, *Quart. Journ. Geolog. Soc.* 18, 418).

Methods of *fractional analysis* have been introduced for the purpose of effecting a chemical separation of the constituents of certain rocks. Gmelin, in his analyses of phonolites, was perhaps the first to separate the part soluble in hydrochloric acid from that which was insoluble, and to analyse each separately. Grave objections may, however, be urged against this method, and it is now rarely used. More trustworthy results have been obtained by treating the rock, if composed of various silicates, with hydrofluoric acid, which attacks the several minerals in unequal degree. Such a method is sometimes useful in controlling a bulk-analysis.

Of late years considerable use has been made of certain dense liquids for the purpose of effecting the mechanical separation of the minerals which compose a rock, in order that each constituent may be isolated in a state of purity for separate analysis. The S.G. of the liquid is so adjusted that when the rock is coarsely powdered and thrown into the liquid certain of the minerals float while others sink. Several such liquids are now in common use in the geological laboratory (*v.* J. W. Judd, *Proc. Geolog. Assoc.* 8, 278; and F. Rutley, *Rock-forming Minerals*, London, 1888).

Sonstadt's solution, recommended by Church, consists of a solution of HgI_2 and KI; it may be obtained with S.G. 3·196 (*C. N.* 29, 127; *Neues Jahrb. f. Min.*, Beilage 1, 179). It is also known as Thoulet's solution. If a rock consisted of plagioclase with S.G. 2·7 and augite with S.G. 3·1, and these minerals were set free by mechanical disintegration of the rock, a complete separation might readily be effected in Sonstadt's solution with S.G. of about 3. The poisonous and corrosive character of the solution, however, tends to limit its use. Klein's solution is a boro-tungstate of cadmium, less dangerous than Sonstadt's, and capable of attaining to a higher S.G., the maximum being about 3·6. The solution has, however, the disadvantage of being decomposed by carbonates, and therefore if these be present in the rock they should be removed before the solution is used (*Bull. Soc. Min. France*, 4, 149). Rohrbach's solution resembles Sonstadt's, but contains BaI_2 in place of KI; its maximum S.G. is 3·58. It is unfortunately decomposed in the presence of water, so that all minerals used must be perfectly dried (*Neues Jahrb.* 11, 186). Brauns has recommended the use of methyl iodide, which has S.G. 3·337 at 10°. Bréon advocates the employment of fused $PbCl_2$, either alone or mixed with $ZnCl_2$; but though by properly adjusting the proportions of the constituents it may be prepared of high S.G., its use in a state of fusion is attended with much inconvenience (*Bull. Soc. Min. France*, 3, 46).

The S.G. of a heavy solution may be conveniently determined by means of Westphal's hydro-balance (*Neues Jahrb. f. Min.* 2, 87). The S.G. of very small fragments of minerals and rocks may thus be accurately taken: the fragments are placed in the dense solution, which is then diluted until they remain suspended indifferently in any part of the liquid (*v.* also W. J. Sollas, *Proc. R. Dublin Soc.*, Jan. 19, 1885). The separation of one mineral from another, when in small particles, is best effected in a special type of separating funnel, devised by Harada and improved by Brögger. (For the subject generally *v.* Rosenbusch, *Mikroskop. Physiog.* 2 Aufl. Bd. i. [Stuttgart], 1885, pp. 194, 215; English translation by Iddings, 1888. p. 91.)

The mechanical separation of the constituent minerals of a rock, previous to chemical analysis, is aided by the use of a powerful magnet. With an electro-magnet of great power, silicates rich in iron, such as hornblende, augite, and biotite, may be picked out of the pulverised rock (Fouqué a. Lévy, *Min. Micrograph.* [Paris, 1879], 115). (For a large collection of analyses of rocks consult J. Roth, *Die Gesteins-Analysen* [Berlin, 1861], and his *Beiträge*, 1873–84.)

Micro-chemical examination of rocks.—The microscopic examination of thin sections of rocks, which forms an important branch of modern petrography, has led to the introduction in recent years of certain micro-chemical tests for distinguishing one mineral species from another. The micro-chemical methods do not aim at effecting a complete analysis of the microscopic constituents of a rock, but are used rather for the purpose of controlling optical determinations.

The rock may be coarsely powdered in a steel mortar, and the particles to be examined after separation of the fine powder by a sieve may be picked out by aid of the forceps, or if too small may be removed on the point of a needle moistened with glycerine, from which the accumulated grains may be detached by dipping the needle into water. Any steel particles derived from the mortar may be separated by a magnet. In other cases the constituent minerals are so minute that it becomes necessary to prepare a thin section of the rock and subject it to examination under the microscope. By means of a needle, the grains to be examined may be picked out from the section. It is convenient for the operator to commence by detaching the fragments near the edge, and to work patiently thence towards the centre of the section. The section is, of course, not protected by a cover-glass; and the Canada balsam by which the slice is cemented to the glass is dissolved off by treatment with alcohol.

In some cases the particles to be examined cannot conveniently be separated, and it then becomes necessary to attack the mineral in the section itself. The particular mineral to be tested is brought into the field of the microscope, and a perforated cover-glass is then drawn over the section in such a way that the mineral is just under the perforation. Through this aperture the balsam is dissolved, and the mineral exposed ready for attack by the reagent. If hydrofluoric acid is to be used the section is covered with a perforated slip of platinum foil instead of a cover-glass. By means of a pipette a drop of the solvent is lodged on the slide, and the liquid may then be conducted to the mineral exposed at the aperture by the point of a platinum wire.

The general method in these micro-chemical reactions is to produce certain compounds which present distinctive crystalline forms capable of recognition under the microscope. In Boricky's method the microscopic minerals are attacked with H_2SiF_6Aq, which forms a series of crystallised silicofluorides, many of which are sufficiently characteristic in form to be readily recognised. Uncertainty is, however, introduced by the fact that several of the silicofluorides are isomorphous. Behrens attacks the rock with HFAq, and treats the product with H_2SO_4Aq. In Streng's processes most of the salts crystallise out as chlorides. For the special reactions, and for figures of the microscopic crystals produced by these reactions, reference may be made to Klement a. Renard, *Réactions Microchimiques*, Brussels, 1886; Haushofer, *Mikroskopische Reactionen*, Munich, 1885; Behrens, *Mikrochemische Methoden zur Mineralanalyse*, Vers. en Med. d. k. Ak. Wetensch., Amsterdam, 1882; and G. Boricky, *Elemente einer neuen chem.-mik. Min.- u. Gesteinsanalyse* Arch. d. naturw. Landesfor. v. Böhmen, Prague, 1877.

The geological chemist is often called upon to decide the nature of a given felspar in a rock, and for this purpose the method introduced by Szabó of Budapest is convenient. An extremely small particle of felspar is introduced into the flame of a Bunsen burner provided with a special chimney of sheet-iron. The proportion of soda or potash may be approximately determined by comparing the extent of the yellow or red colouration with the standard plates issued by Szabó. In experienced hands this process yields remarkably precise results (*v.* Szabó, *Ueber eine neue Methode, die Feldspathe in Gesteinen zu bestimmen*, Budapest, 1876; and F. Rutley, *Rock-forming Minerals*, London, 1888, p. 9).

Classification of Rocks.—Some rocks have evidently been formed as deposits in a watery medium, while others have existed at some period at a high temperature and been more or less completely fused; hence arise two great groups of rocks: one of *aqueous*, the other of *igneous*, origin. Certain rocks, whether aqueous or igneous, have suffered such alteration since their formation that their original characters are no longer to be recognised by direct observation, and hence these are known as *metamorphic* rocks. Of the so-called aqueous rocks a few have been deposited directly from solution as chemical precipitates; but by far the larger number have been thrown down as sediments from a state of mechanical suspension. The aqueous deposits are known as *sedimentary* or *stratified* rocks, while the igneous rocks are often described as *unstratified* or *massive*. In addition to these types there are a few rocks, like coal and certain limestones, which owe their origin, directly or indirectly, to organic agencies, and are hence termed *organic* rocks. But though the ultimate origin of such deposits is organic, the changes through which they have passed in reaching their present condition are essentially chemical.

It usually happens that several modes of formation have contributed to the production of a single rock. Thus, rocks formed as chemical precipitates, though practically homogeneous, may contain an admixture of foreign matter representing material that was mechanically thrown down during precipitation. On the other hand, a sedimentary rock frequently has its constituent grains bound together by mineral matter which has been precipitated in association with, or subsequent to, the mechanical deposit, and has acted as a cementing medium; a sandstone, for example, may have its component grains united by mineral matter precipitated from solutions percolating through the original mass of sand. (On the origin and classification of rocks, consult A. Geikie, *Text-book of Geology*, 2nd ed., 1885; A. H. Green, *Physical Geology*, vol. i., 3rd ed., 1882; J. J. H. Teall, *British Petrography*, 1888; A. de Lapparent, *Traité de Géologie*, 2nd ed., Paris, 1885; and H. Credner, *Elemente de Geologie*, Leipzig, 3rd ed., 1876.)

In dealing with igneous rocks it is always desirable to ascertain the proportion of silica in the rock as a whole, since a common classification of such rocks is based upon this datum. Bunsen, in studying the rocks of Iceland, suggested that all igneous rocks have been formed by admixture of two magmas which he termed the *normal trachytic* and *normal pyroxenic* (*P.* 83, 197). Durocher afterwards developed a theory which derived the rocks from two magmas situated at different subterranean depths, termed by him *acid* and *basic*, and practically corresponding respectively with the trachytic and pyroxenic magmas of Bunsen (Durocher, *Essai de Pétrologie comparée*, Ann. de Mines, 40, 1857, pp. 217, 676). At the present time most petrographers define the *acid* or *light* rocks as those containing from 65 to 80 p.c. of silica, and having S.G. 2·3 to 2·7; they usually contain a high proportion of alkalis, especially potash, and but a small percentage of lime, magnesia, and oxides of iron. On the other hand, the *basic* or *dense* rocks contain only from 45 to 55 p.c. of silica, but have S.G. rising from 2·5 to as high as 3·1; they are characterised by a low percentage of alkalis, with more soda than potash, and by a high percentage of lime, magnesia, and oxides of iron (*v.* Teall, *Brit. Pet.*, cap. ii.; and on the classification of igneous rocks, Bonney's anniversary address, *Geol. Soc.*, 41, 1885).

Chemically-formed Rocks. — The chemical precipitates which are of interest to geologists, as having been formed on a large scale in nature, belong chiefly to the groups of carbonates, sulphates, and chlorides, represented respectively by such rocks as limestone, gypsum, and rock-salt. Perhaps the simplest example is offered by *rock-salt*, since this has been formed by the mere evaporation of a natural brine. On the composition of sea-water—a subject of much interest to the geological chemist—*v.* Dittmar, *Rep. of Challenger*, 1884; Forchhammer, *T.* 155, 203; J. Roth, *Allgemeine u. Chemische Geolog.*, Bd. 1 [Berlin, 1879]; and Bischof, *Chem. u. Phys. Geolog.*, 2nd ed., Bd. 1 [Bonn, 1863], p. 426.

Rock-salt has usually been formed in inland sheets of salt-water. These are either isolated portions of the sea or the relics of lakes which were originally fresh but have acquired salinity by the accumulation of salts introduced by river-waters. The great Salt Lake of Utah, situated in an area of inland drainage, receives streams which bring in salt; but, having no outlet, the waters tend to become concentrated. In this arid region evaporation is rapid, and along the shallow margin of the lake vast quantities of common salt spontaneously crystallise during the dry season; while in winter, whenever the temperature falls below $-6·5°$ Na_2SO_4 is ppd., the quantity of this salt formed in a single season amounting to thousands of tons. Many ancient lakes have in the course of time completely disappeared by desiccation, and their position is now marked by extensive saline deposits. For the chemical history of a fossil lake, see J. C. Russell's 'Lake Lahontan' in *Monographs of U. S. Geolog. Surv.* 1885.

On the evaporation of a salt-lake, or saline lagoon, the least soluble salts will tend to crystallise first, the order in which the salts are successively deposited being inversely as the order of their solubility. Such a process of fractional crystallisation in nature is illustrated by the remarkable salt-deposits at Stassfurt in Prussia. In the lowest beds the rock-salt is associated with gypsum, anhydrite, and carbonate of calcium; but above the rock-salt there are deposits of deliquescent compounds, rich in potassium and magnesium, which remained in the mother-liquor after the NaCl had separated. The association of the rock-salt and anhydrite in alternate layers has led to the suggestion that they represent seasonal deposits, the former having been deposited in the warmer, and the latter in the colder, parts of the year. The soluble salts above the main mass of rock-salt, known locally as *Abraumsalze*, consist chiefly of polyhalite ($K_2SO_4.MgSO_4.2CaSO_4.2H_2O$), kieserite ($MgSO_4.H_2O$), and carnallite ($KCl.MgCl_2.6H_2O$); *v.* Bischof, *Die Steinsalz bei Stassfurt*, 2 Aufl. 1875; Ochsenius, *Die Bildung der Steinsalzlagen*, 1877; Precht, *Die Salzindustrie von Stassfurt*; Bauerman, *Proc. Civil Eng.* 88, 415; and C. Napier Hake, *S. C. I.*

Origin of Limestone.—One of the commonest examples of a chemically-formed rock is afforded by certain deposits of *limestone* which have been ppd. from calcareous waters. Such are the deposits known as *calcareous sinter* or *tufa*, so commonly formed by springs flowing through limestone districts, and forming in some cases important rock-masses, like the *travertine*, or 'Tibur stone,' of Tuscany. But while certain limestones are the result of direct ppn., it appears that by far the greater number of such rocks owe their origin to organic agencies. Such, for instance, is the chalk which is largely made up of the calcareous tests of foraminifera; such, too, are the coral-limestones, which are formed in large measure of the hard corallia of certain actinozoa. On the nature and origin of limestones, *v.* H. C. Sorby's Presidential Address to the Geolog. Soc., 1879 (*Quart. Journ. Geol. Soc.* 35, 56, 'Proc.'); also F. Senft, 'Die Wanderungen u. Wandelungen d. Kohlens. Kalkes' (*Zeitsch. d. deutsch. Geolog. Ges.*, 13, 1861, 263).

When $CaCO_3$ is deposited from thermal springs, the pp. usually takes the form of *aragonite*, the orthorhombic species of $CaCO_3$, harder and denser than calcite. The ppn. of aragonite is well illustrated by the *Sprudelstein* of Carlsbad. The water in which this is formed has a temperature of about 73°C., and though containing only 0·29 p.c. of $CaCO_3$, it readily deposits this salt on cooling. The sprudelstein is commonly oolitic or pisolitic, each little sphere being formed of a series of concentric layers deposited successively around a nucleus, and thus imitating the oolitic structure familiar to geologists in various limestones. The experiments of G. Rose tended to show that when a solution of carbonate of calcium is warm or concentrated it deposits aragonite, while if cold or very dilute it throws down calcite. It has been shown by Credner that the deposition of aragonite is favoured by the presence of gypsum, strontianite, and certain other foreign bodies in the solution from which ppn. proceeds.

Calcareous matter deposited on a large scale is usually more or less impure, and hence limestones become argillaceous, bituminous, &c. On the solution of a limestone by natural solvents, a variable amount of insoluble matter is left, and where the action has extended over long periods the residual impurities, by their accumulation, may acquire considerable importance: such, for instance, is the origin of the deposits on the chalk in this country known as 'clay-with-flints;' and the reddish earth so common in limestone caverns and known as 'cave-earth.' On the solution of limestones in nature, *v.* T. Mellard Reade, *Chemical Denudation in relation to Geological Time* [London, 1879].

Origin of Dolomite.—The origin of magnesian limestone, or *dolomite*, has long been a chemical enigma. Since dolomite frequently occurs in association with rock-salt, it has been suggested that it must be of lacustrine origin. Bischof, however, showed long ago the difficulty of simultaneously ppg. $CaCO_3$ and $MgCO_3$ from a solution containing these salts. At the beginning of the evaporation $CaCO_3$ alone falls; towards the close of the process $MgCO_3$ alone; and it is only at intermediate stages that the mixed carbonates are thrown down. It might, therefore, be expected that the geologist would find pure limestone below, succeeded by a deposit of dolomite, and followed above by pure magnesite—a sequence, however, which is not observed in nature. Indeed, dolomite seems to have been formed not so much by direct ppn. on the evaporation of waters in which the two carbonates co-existed as by certain chemical reactions.

Sterry Hunt has pointed out that the interaction between carbonate of sodium and the chlorides of magnesium and calcium in sea-water would give rise to dolomite, with simultaneous production of chloride of sodium, thus explaining the common association of dolomite with rock-salt. There seems no difficulty in providing the necessary quantity of Na_2CO_3, inasmuch as various soda-bearing silicates, notably the soda-felspars, are commonly suffering decomposition in nature by the action of carbonated waters, with consequent formation of Na_2CO_3 and separation of silica. Another reaction suggested by Sterry Hunt is that which may occur between $CaCO_3$ and $MgSO_4$; the resulting $MgCO_3$ may, under certain conditions, become associated with fresh $CaCO_3$, so as to form dolomite, which will then be accompanied by a precipitate of $CaSO_4$. As a matter of fact, nothing is more common than to find dolomite naturally associated with gypsum (*Chem. and Geol. Essays*, 1875, 90).

Hoppe-Seyler obtained dolomite by heating carbonate of calcium in a solution of bicarbonate of magnesium in a sealed tube at 100°C. (*Zeits. deutsch. geol. Ges.* 27, 509). Possibly in some cases dolomite has been formed under abnormal conditions of temperature. The crystalline dolomites, enormously developed in the triassic series of the Eastern Alps, are believed to be metamorphic rocks, or ordinary limestones which have become dolomitised (*v. infra*).

Weathering of Rocks.—Most rocks on or near the surface of the earth have suffered more or less chemical change by the natural action of air and water. This weathering usually takes the form of *oxidation* and *hydration*; thus, rocks such as basalt, which contain minerals rich in iron, exhibit along their joint-planes a rusty appearance, due to the formation of ferric hydrate. Deposits of brown iron-ore of great magnitude may result from the alteration of masses of iron-pyrites. Such, too, is the origin of the *gossan*, or impure brown iron-ore commonly found in the upper part of mineral veins where anogenic action has been rife, and known to Continental miners as the *Chapeau de fer* or *Eiserne Hut*. Many clays and other rocks present in their unaltered condition a bluish or grey colour, due to the presence of finely-disseminated iron-pyrites, which in like manner decomposes on exposure, yielding ferrous sulphate, and finally ferric hydrate, and the rock thus assuming brown and yellow tints. (On the colour of certain oolitic rocks *v.* A. H. Church, *C. J.* [2] 2, 379.)

On the other hand, a process of *deoxidation* may frequently be traced in the natural alteration of rocks and minerals, the principal reducing agent being organic matter. Sulphates may thus be reduced to sulphides; whence in many cases the origin of iron-pyrites—a mineral commonly found in association with coal, fossil wood, shells and other organic remains (*v.* Pepys, *Trans. Geol. Soc.* 1, 399). In like manner gypsum may be reduced to the condition of sulphide of calcium; and this, if dissolved in water containing carbonic acid, will yield carbonate of calcium and sulphuretted hydrogen, the latter readily depositing free sulphur on exposure to the air. Hence probably the origin of the associated deposits of gypsum, sulphur, and limestone, so familiar to the geologist in Sicily and other sulphur-bearing localities. The removal of crystals of selenite from clays and other rocks may be due to similar reactions and not to mere solution (Duncan, *Q. J. Geol. Soc.* 22, 12)

It has long been known that the organic acids resulting from the decomposition of vegetable matter may exert a bleaching action upon red and brown rocks, by reducing the ferric oxide to a lower state of oxidation. It has been suggested that some of the finest white glass-making sands may have been derived from sands originally yellow or brown, but decolourised in this way. At the same time such reducing action appears incompetent to explain the local decolouration observed in many variegated rocks (*v.* an important paper by G. Maw in *Q. J. Geol. Soc.* 24, 351).

Hydration, though usually accompanying oxidation, may occur in nature without any other chemical change. A common illustration of such action is seen in the conversion of anhydrite into gypsum, by absorption of two molecules of water. This change is accompanied by a marked increase in bulk, 1 vol. of $CaSO_4$ becoming 1·6 vol. of $CaSO_4.2H_2O$. The galleries of deserted mines in which anhydrite has been worked have become closed by the swelling of the walls, consequent on hydration of the mineral. Geologists believe that a similar increment of bulk, occurring on a large scale in deep-seated deposits, may account for certain minor movements of the Earth's crust.

Origin of Kaolin.—It is commonly said that one of the most striking examples of weathering is afforded by the decomposition of the felspar in granitic and other rocks. Meteoric waters, containing carbonic and organic acids, readily attack felspathic minerals, removing the alkalis in a soluble form, while the silicate of aluminium, in a hydrated condition, remains behind as clay. *Kaolin*, or china-clay, the purest form of argillaceous matter, may thus be derived from felspar-bearing rocks, especially granites. It was seriously held that the great heat experienced in working the Comstock lode was due to the kaolinisation of the felspars in the surrounding rocks—a suggestion, however, entirely disproved by experiment. In Cornwall it is not uncommon to find granite in which the orthoclase, or potash-felspar, is more or less decomposed, while the associated silicates remain almost unaltered: such a rock is known as *china-stone* or *petunzite*; while a rock in which the felspar is entirely kaolinised is termed *china-clay rock* or *carclazite*. It is frequently held that the simple action of meteoric waters, charged with carbonic and organic acids, is sufficient to explain the origin of kaolin; but though kaolinisation may undoubtedly result from mere weathering, it seems that superficial action is incompetent to explain all the observed phenomena. The change appears rather to have been effected by means of solutions derived from deep-seated sources, circulating in the joints of the granite. It has often been pointed out that the decomposed granite is associated with minerals containing fluorine (like lepidolite) or fluorine and boron (like schorl). Von Buch in 1824, and Daubrée in 1841, suggested that the change has been due to hydrofluoric acid or other fluorides, which, acting upon the granite at an elevated temperature, would decompose the felspar, removing its alkali as a fluoride. Cassiterite (SnO_2) is a common associate of the kaolinised granite, and there is reason to believe that this mineral has been produced by the agency of fluorine. Daubrée succeeded in producing crystals of SnO_2 by passing the vapour of stannic chloride with steam through a heated porcelain-tube, the chloride having been used in place of the fluoride merely for convenience (*v.* Daubrée's *Études synthétiques de Géologie expérimentale*, Paris, 1879, where his researches are presented in a collected form. For Cornish kaolin *v.* J. H. Collins, *The Hensbarrow Granite*, Truro, 1878; and *Mineralog. Mag.* **7**, 205).

Metamorphism.—A rock, whether of aqueous or of igneous origin, is said to be *metamorphic* when it has been altered not by atmospheric agencies but by some profounder influence which has so affected its structure and composition that its original character is no longer to be recognised by direct observation. Thus the intrusion of an igneous rock among sedimentary strata may give rise to changes known as *contact metamorphism*. By such action an ordinary limestone may be converted into a crystalline marble—a phase of metamorphism conveniently distinguished by A. Geikie as *marmorosis*. The production of a saccharoidal marble from an amorphous limestone under the influence of heat and pressure was illustrated by James Hall's experiments in the early part of this century.

The effects of contact metamorphism are partly physical and partly chemical. To the former class may be referred not only the crystallisation of limestone but the induration and even fusion of various other rocks, and the development of prismatic structure in the neighbourhood of the heated mass. Among ordinary chemical effects may be noted the expulsion of water, the reddening of a calcined rock and the conversion of coal into a natural coke. But the most interesting phenomena are those attending the development of new minerals. Thus, a slate in the neighbourhood of an intrusive granite frequently contains garnets, chiastolite, and other crystallised silicates; while metamorphic limestones may inclose rock-crystal, garnets, idocrase, micas, and other minerals which appear to have been produced by the rearrangement and crystallisation of the materials of the sand, clay, and other impurities originally present in the limestone. The ejected limestone blocks of Monte Somma, consisting originally of the Subapennine limestone, are rich in minerals of this character, and have lately been specially studied by J. H. Johnston-Lavis, of Naples, and by B. Mierisch (*Min. u. Pet. Mitt.* [N. F.] 8, 113 [1887].)

When metamorphic rocks extend over a wide area and are not visibly associated with igneous rocks to which their alteration may be referred, they are said to be due to *regional metamorphism*. The agencies by which such phenomena have been produced are exceedingly obscure, but while many of the changes are of a chemical and molecular character, it is evident that molar forces have been operating on a large scale. Of late years it has been recognised that the mechanical movements of the rocks have largely contributed to the production of the characteristic structures in those metamorphic rocks known as the crystalline schists, not only producing deformation of the constituent minerals, but indirectly causing the passage of one mineral into another. (On dynamic metamorphism *v.* J. Lehmann, *Enstehung d. altkrystallinischen Schiefer-Gesteine*, Bonn, 1884; Teall's *Brit. Petrog.*, 1888, cap. xiv.; *Études sur les schistes crystallins*, Int. Geol. Congress, 1888; A. Harker, *B. A.* 1885.845. For contact-metamorphism, *v.* Delesse's *Études sur le métamorphisme des Roches*. For the subject generally consult Bonney's address to Geol. Soc., *Quart. Journ. Geol. Soc.*, 42, 55; and A. Irving, *Rock-metamorphism*, 1888.)

Hydrothermal action.—The effects of thermal metamorphic agencies, even in the neighbourhood of an igneous rock, are usually due, not so much to dry heat as to hydrothermal action. Although pure water at ordinary temperature and pressure is capable of slowly dissolving the common mineral-constituents of rocks (Rogers, *Am. S.* [2] 5, 401), its solvent action is vastly increased by the great heat and pressure to which it must be subjected in the deeper-seated portions of the earth's crust, where metamorphism probably has its normal seat. Such action is well illustrated by the remarkable experiments of Daubrée. This observer found that when water was heated in strong glass tubes inclosed in thick wrought-iron cylinders, and exposed uninterruptedly to a temperature of at least 400°C. for several weeks, the glass was transformed into a hydrated silicate, analogous to a natural zeolite, while the interior of the tube became lined with a crust of small transparent crystals of quartz (*Géolog. expérim.* 163). In some cases the artificial crystals of quartz lined the walls of the tube like the quartz in a natural geode (*ib.* 166).

The solvent action of water at great depths accounts for the peculiar composition of the water of geysers. Under enormous pressure and at a high temperature these waters are capable of decomposing the volcanic rocks which they traverse and of dissolving out silica. Thus, water from the Opal Spring in the Yellowstone National Park contained as much as 53·76 g. of silica to the imperial gallon (Leffmann). On the evaporation of such water the silica is deposited in a hydrated form as a kind of opal or siliceous sinter, known as *fiorite* or *geyserite* (*v.* A. C. Peale, 'Thermo-hydrology,' in *Twelfth Rep. U.S. Geol. and Geog. Survey of the Territories*, 2).

Dolomitisation.—Among cases of metamorphism, that of the alteration of a normal limestone into dolomite has long been recognised and variously explained. Von Buch and certain other German geologists, looking at the association of crystalline dolomite with basic igneous rocks in the Tyrol, held that these erupted masses had emitted vapours containing compounds of magnesium which had acted upon the neighbouring limestone, causing dolomitisation. In support of such a view it was pointed out by Durocher (*C. R.* 23, 64) that when fragments of limestone are heated with $MgCl_2$ in a closed vessel, the limestone is partially converted into dolomite. Such an action, however, if it occurs at all in nature, must be limited to the immediate neighbourhood of the heated body evolving the magnesian vapours. In order to explain the alteration of large masses of limestone it is simpler to invoke the agency of percolating water holding compounds of magnesium in solution. Even where limestone has been dolomitised in contact with basalt, Bischof contended that the change was due to the action of water containing $MgCO_3$ resulting from the decomposition of the magnesian silicates in the igneous rock.

When water containing carbonate of magnesium percolates through a limestone, the magnesian salt tends to unite with part of the calcium carbonate so as to form a double salt, while $CaCO_3$ is at the same time dissolved out. For every molecule of $CaCO_3$ removed, a molecule of $MgCO_3$ is introduced, the change being accompanied by a diminution of volume to the extent of 12 or 13 p.c. Now it is a remarkable fact that natural dolomites are frequently marked by a cellular or cavernous texture, and Elie de Beaumont long ago suggested that the cavities were due to shrinkage consequent on dolomitisation. It is estimated that in many magnesian limestones the hollows represent about 12 p.c. of the bulk of the rock. The sulphate and chloride of magnesium in sea-water may also transform limestone into dolomite, but according to Favre the action requires a temperature of 200°C. favoured by great pressure. (For a good review of the whole subject of dolomitisation *v.* A. H. Green's *Geology*, 3rd ed. 1882. 408; also Doelter a. Hoernes, 'Chem.-Genet. Betracht ü. Dolomit,' in *Jahr. d. k.-k. Geol. Reichs*, 1875. 25, p. 293; with a full bibliography to date.)

$MgCO_3$ is not the only carbonate which has been introduced into certain limestones by secondary processes. In some cases beds of limestone have been more or less completely transformed into $FeCO_3$—a change well illustrated on a large scale in the important deposits of Cleveland ironstone in the Middle Lias of N.E. Yorkshire. Sorby believes that this ore has been formed from an oolitic limestone by percolation of water containing bicarbonate of iron in solution. Most of the fossil shells associated with the ore have suffered a like conversion, and in some cases the ferrous carbonate has been further changed into ferric hydrate (*Proc. Geol. and Polyt. Soc. W. Riding*, 1856-7).

Serpentinisation.—The origin of serpentine has been a subject of much discussion, in which the geologist has had to appeal to the chemist. By most modern petrographers it is regarded as an altered eruptive rock, having been derived mainly from olivine. Pseudomorphs of serpentine after olivine are familiar to the mineralogist, and an action similar to that which produced this alteration appears to have been concerned in the metamorphism of large rock-masses. This view has gained much credence of late years by the study of the microscopic structure of serpentine by Sandberger, Tschermak, Bonney, and other petrographers. Hydration is effected by water gaining access to the olivine through the irregular fissures by which the mineral is usually traversed; and in the case of ferriferous olivines the iron is deposited in the form of magnetite and limonite (*v.* Teall, *Brit. Petrog.*, 1888, p. 104).

While many serpentines suggest by their occurrence as dykes and bosses that they have been derived from eruptive rocks, others occur in beds intercalated among crystalline schists, especially in association with limestone. It has been supposed that such serpentine may have resulted from the alteration of dolomite or some other magnesian rock of aqueous origin. Sterry Hunt, who is specially familiar with the serpentines of the Laurentian series of Canada, has always argued against the derivation of serpentine from igneous rocks, and regards it simply as a product of direct precipitation from natural waters. He holds that by the decomposition of the various crystalline silicates in nature, soluble silicates of the alkalis and of lime are set free, and passing into streams are ultimately mixed with waters rich in magnesium salts—such as the sulphate or chloride in sea-water—when double decomposition ensues, and silicate of magnesium is precipitated in a gelatinous condition (*Trans. R. Soc. Canada*, 1, 165; *Mineral Physiology*, Boston, 1886, p. 427).

Recent formation of minerals.—Observations on the production of minerals under known conditions in historic times are of much interest to the geological chemist, inasmuch as they suggest the processes which may have operated in nature during geological time. Daubrée long ago called attention to the production of a series of minerals since the Roman period at the hot springs of Plombières in the Vosges. Around these springs the Romans had built walls of concrete, consisting of brick and stone cemented by mortar. By the action of the waters at 50° C. upon the concrete, there has been formed a series of minerals including chabazite, harmatome, mesotype, and other zeolites, associated with opal, calcite, &c. Similar effects have been observed at other Roman baths, as at Luxeuil (Haute Saône) and at Bourbonne-les-Bains (Haute Marne) (*v. Géologie Expérimentale*, p. 179; and Percy's *Lectures on Chemical Geology* in *C. N.* 9, 100).

Geodes.—The production of certain minerals at the Roman stations just cited recalls the natural formation of similar substances in the cavities of basaltic and other rocks. These cavities, though perhaps in some cases due to the removal of pre-existing crystals by solution, usually represent bubbles produced by the disengagement of gas or steam at a time when the igneous rock was in a plastic condition. The minerals occurring in such cavities are of secondary origin, having been introduced through the medium of solutions permeating the rock long after solidification. When the vesicles are filled with mineral matter the rock is said to be *amygdaloidal*; if the cavities are not completely filled, and the walls are lined with crystals, they are termed *geodes*. The most common of these secondary minerals are calcite and silica, the latter frequently forming agates. In an agate, regular layers of colloidal, crypto-crystalline, and crystalline, silica, succeed each other with regularity. The exact manner in which the silica has been introduced, and precipitated on the walls, has given rise to much discussion, but a clue is suggested by the experiments of Pankhurst and I'Anson on the artificial production of agates (*Mineral Mag.* v. 34).

Origin of Mineral Veins.—The deposition of secondary minerals in the cavities of rocks tends to throw light upon the formation of mineral veins, or lodes—a subject on which the geologist has frequently appealed to the chemist. It is now generally held that these veins represent fissures filled in by deposition of mineral matter from a state of solution. The chief difficulty is to trace the metalliferous minerals to their origin. The most promising modern researches are those of Prof. Fridolin Sandberger, of Würzburg (*Untersuchungen über Erzgänge*, i. 1882; ii. 1885). By comparative analyses of the ore, the veinstone, and the country rock, he has shown that the contents of the lode have been derived in certain cases from the neighbouring rocks, and that the ores have probably obtained their metallic elements from the common constituents of the crystalline rocks, which had not previously been suspected to contain such metals. Analyses of ordinary rock-forming minerals, like mica, augite, hornblende, and olivine, revealed the presence in them of a large number of the heavy metals. Nor is it only in the crystalline rocks that such metals occur, Dieulafait having shown that many of them are widely distributed in minute proportion through the stratified rocks. Such an occurrence is readily explicable by the fact that most sedimentary strata have been derived, directly or indirectly, from the disintegration of the older crystalline rocks. Thus it has been shown by A. Dick that minerals containing zirconium and titanium are widely distributed through sands of tertiary age (*Nature*, 36, 91), and Teall has found similar minerals in various clays (*Min. Mag.* 7, 201).

Some interesting phenomena tending to illustrate the origin of certain mineral veins have been studied in districts in California and Nevada, where hydrothermal action is rife. Hot water, steam, carbonic acid, sulphuretted hydrogen, and other gases escape from fissures in volcanic rocks, and on the walls of these fissures they deposit siliceous sinter associated with free sulphur, cinnabar, iron-pyrites, and other metalliferous minerals, including metallic gold—the whole assemblage being suggestive of the contents of certain veins (*v.* A. J. Phillips, *P. M.* 1868. 321; Laur, *Ann. d. Mines*, 3, 423).

Durocher and some other observers have argued in favour of many metallic minerals in lodes having been produced by sublimation. In Durocher's experiments he succeeded in producing galena, iron-pyrites, zinc-blende, and other metallic sulphides by passing certain vapours through glass tubes at a high temperature (*C. R.* 33, 823; 42, 850).

As an illustration of the production of thin strings of metallic minerals by decomposition of vapours, attention may be called to the frequent occurrence of specular iron ore sublimed in the crevices of lava, this mineral having obviously been formed by the reaction of steam and ferric chloride: $Fe_2Cl_6 + 3H_2O = Fe_2O_3 + 6HCl$. (On the general subject of mineral veins, *v.* J. A. Phillips, *Ore Deposits*, London, 1884; Von Cotta, *Erzlagerstätten*, Freiberg, 1859 [Translation by F. Prime, New York, 1870]; and Von Groddeck, *Lagerstätten der Erze*, Leipzig, 1879.)

Chemistry of the Volcano.—The chemical operations involved in volcanic phenomena are extremely obscure. It is generally admitted that water is the prime factor in the production of these phenomena, and as the temperature prevailing at volcanic foci probably exceeds the critical point of water it must exist in the form of vapour, notwithstanding the enormous pressure to which it is subjected: possibly the temperature is so high that the water is dissociated. Fouqué found in the lava of Santorin of 1876 a notable quantity of free hydrogen co-existing with free oxygen. The volcanic vapours, associated with steam are chiefly HCl, SO_2, CO_2, H_2S, free O, H, and N, and sometimes NH_3 and CH_4. The HCl may be due to access of sea-water, most volcanoes being situated on islands, or, if on the mainland, near to the sea-coast. Ricciardi has found that finely powdered granite and lava mixed with pure NaCl evolve HCl when heated, the quantity being increased by blowing in a current of steam (*Gazzetta*, 16, 38). The sublimed products of volcanic rocks include a large number of metallic chlorides, notably those of NH_4, Na, Fe, Cu, Ca, and Mg.

The SO_2 of volcanic exhalations has been referred by Ricciardi to the reaction of silica with $CaSO_4$ and $MgSO_4$, whereby silicates are produced, with separation of sulphur trioxide which is resolved into sulphur dioxide and oxygen. He found that granite mixed with the sulphates cited above would evolve SO_2 when heated. By the interaction of SO_2 and H_2S free sulphur is produced and deposited as an incrustation on the lava. By oxidation, sulphuric acid is developed, and this by its action on the volcanic rocks tends to decompose them, with production of various sulphates. Thus it comes about that alum is manufactured in the crater of Vulcano, one of the Lipari Islands, and at the Solfatara, near Naples. The term 'solfatara' is now used by geologists as a general designation for a volcano which is approaching extinction and emits only vapours. Long after other emanations cease, CO_2 may be exhaled, as in many localities in the Eifel and in Auvergne. Boric acid, in a finely-divided condition, is produced from the nearly exhausted crater of Vulcano, and from the *mofette* of Tuscany where it has long been utilised industrially. (On the general subject of volcanoes, *v.* Judd's volume in the International Science Series.)

Synthesis of Igneous Rocks.—The artificial reproduction of many igneous rocks has been successfully accomplished in recent years by Fouqué and Lévy in the geological laboratory of the Collège de France, in Paris. (For a full description of these researches, *v.* their *Synthèse des Minéraux et des Roches*, Paris, 1882.) These observers have shown that a number of basic eruptive rocks can be formed by the fusion of their constituents, and that the products, examined in thin sections under the microscope, are identical in structure and composition with the corresponding natural rocks. It had previously been supposed that water, in some form, played a conspicuous part in the liquefaction of igneous rocks, and that this was in fact due not to dry fusion but rather to hydrothermal action. The syntheses performed by Fouqué and Lévy controverted this view, inasmuch as they were effected solely by dry igneous fusion, without the presence of water or any other volatile medium, and without flux or other chemical agent.

The raw materials employed by these experimentalists were either the component minerals of the rocks to be produced (such as felspar, augite, &c.), or the chemical constituents of these minerals (silica, alumina, lime, &c.). These materials, corresponding in their relative proportions with the composition of the rock to be imitated, were introduced, in a pulverised condition, into a platinum crucible of about 20 c.c. capacity, furnished with a cover. The crucible was heated in a furnace of Forquignon and Leclerc's type, heated by a Schlösing blowpipe, whereby it could be rapidly raised to a white heat, or reduced at will to a lower temperature, and the heat maintained constant for a long period. The first fusion at a white heat always yielded an isotropic glass, and this if cooled suddenly maintained its vitreous character. But if the fused product was kept for some time at a temperature below a white heat, yet above that of the melting-point of the glass, various crystalline products were developed; and by subjecting the material to successively diminishing temperatures, other products crystallised out, the least fusible being the first to separate.

By a process of fractional crystallisation conducted in this way, Fouqué and Lévy imitated the conditions which appear to have obtained during the formation of volcanic rocks, where the crystallised constituents represent successive periods of consolidation. Artificial basalt was obtained by fusing a mixture of the elements of olivine, augite, and labradorite, and subjecting the resulting black glass to a bright red heat for 48 hours, when the olivine, which is the least fusible component, was found to be crystallised. Then on submitting the mass to a cherry-red heat for another 48 hours, the microlitic crystals of the more fusible minerals separated: these were the lath-shaped crystals of plagioclase and augite, which may be regarded as minerals of the second period of consolidation. Some of the most remarkable experiments were those on the so-called ophites. These are doleritic rocks, in which the augite forms comparatively large plates moulded around the crystals of plagioclase; the former having evidently been of subsequent consolidation to the latter. By a succession of suitable coolings and re-heatings this ophitic structure was perfectly imitated.

Notwithstanding the remarkable success with which the basic igneous rocks have lately been imitated, all experiments on the synthetical formation of the acid rocks have hitherto been fruitless. The reproduction of these natural products forms one of the most interesting fields of investigation left open to the geological chemist. F. W. R.

GEORETIC ACID $C_{12}H_{22}O_4$. A waxy acid obtained from lignite found near Weissenfels. Extracted by 80 p.c. alcohol, and ppd. by $Pb(OAc)_2$; the acid is liberated from the pp. by HOAc (Brückner, *J. pr.* 57, 1). Small needles (from alcohol). Its solution gives a dirty-green pp. with cupric acetate. From similar lignite Brückner isolated resinous leucopetrin $C_{50}H_{84}O_3$ crystallising from alcohol in tufts of needles [above 100°]; geomyricin $C_{34}H_{68}O_2$ [c. 82°] crystallising from alcohol in minute hair-like needles; geoceric acid $C_{28}H_{56}O_2$ [82°]; and geocerin $C_{28}H_{56}O_2$ [80°]. Geocerin is a neutral wax.

GERANIENE $C_{10}H_{16}$. (163°). S.G. $^{\underline{20}}$ ·843. A terpene obtained by treating oil of geranium with P_2O_5 (O. Jacobsen, *A.* 157, 239). By treatment with half the calculated quantity of iodine it is converted into cymene (Oppenheim a. Pfaff, *B.* 7, 625). Gives a liquid hydrochloride.

GERANIOL $C_{10}H_{18}O$. (233°). S.G. $^{\underline{15}}$ ·885. A compound occurring in oil of geranium (O. Jacobsen, *A.* 157, 232; Gintl, *Ph.* [3] 10, 24). Oil. Inactive to light. Fragrant smell like roses. Miscible with alcohol and ether. With calcium chloride at 50° it forms a crystalline compound $(C_{10}H_{18}O)_2CaCl_2$ decomposed by water. Slowly oxidised by air. Potash-fusion forms isovaleric acid. Neutral aqueous $KMnO_4$ forms acetic and isovaleric acids. Even boiling baryta-water slowly forms isovaleric acid. Chromic acid mixture forms also succinic acid. HNO_3 forms nitrobenzene, HCy, oxalic acid, and a resin, but no camphoric acid.

Geranyl chloride $C_{10}H_{17}Cl$. S.G. $^{\underline{20}}$ 1·020. From geraniol and gaseous HCl. Inactive oil smelling like camphor. Alcoholic $AgNO_3$ ppts. even in the cold all the Cl as AgCl. KCy, KCyS, KNO_3, and other K salts displace the Cl by their acid residues.

Geranyl bromide $C_{10}H_{17}Br$. Oil.

Geranyl iodide $C_{10}H_{17}I$. Oil. From the chloride and cold alcoholic KI.

Di-geranyl oxide $(C_{10}H_{17})_2O$. (187°-190°). From geranyl chloride and potassium geraniol $C_{10}H_{17}OK$. Oil, smelling of peppermint.

Di-geranyl sulphide $(C_{10}H_{17})_2S$. From $C_{10}H_{17}Cl$ and alcoholic K_2S. Heavy yellowish oil. With $HgCl_2$ it gives a compound insol. alcohol. When heated it gives geraniene.

GERMANIUM. Ge. At. w. 72·3. Mol. w. unknown, as V.D. has not been determined. [c. 900°] (Winkler, *J. pr.* [2] 34, 177). S.G. $\frac{20\cdot4^\circ}{20\cdot4^\circ}$ 5·469 (W., *l.c.*). S.H. 100°-440° ·0737 to ·0757 (W., *l.c.*). Sharpest lines in emission-spectrum 6020, 5892, 4684·5 (Kobb, *W. A.* 29, 670). L. de Boisbaudran says that the characteristic lines are 4680 and 4226 (*C. R.* 102, 1291).

In 1885 a silver ore from the Himmelsfürst mine, near Freiberg, was recognised by Richter as a new mineral species; to it he gave the name of *argyrodite*. The mineral was carefully analysed by Winkler with the result that the percentages of Ag, S, Hg, Fe, and Zn found added up to 93-94. After much labour, Winkler was able to announce that the rest of the mineral was composed of a new element, to which he gave the name *germanium* (*B.* 19, 210). Winkler was inclined to regard germanium as belonging to the Sb-Bi family, but fuller investigation showed it to be identical with *ekasilicon*, the properties of which had been foretold by Mendelejeff, and the position of which had been indicated by him as group IV., series 5. The reasoning which led Mendelejeff to his statement of the properties of *ekasilicon* was similar to that on which he based his prediction of the properties of *eka-aluminium*, with which element gallium was found to be identical (*v.* GALLIUM, *Chemical relations of*, p. 598).

Occurrence.—Ge forms about 6·9 p.c. of *argyrodite*. The composition of this mineral is approximately expressed by the formula $2Ag_2S.GeS_2$; it contains about ·66 p.c. Fe, ·22 p.c. Zn, and ·31 p.c. Hg. Ge has also been found in *euxenite* to the extent of about 7 p.c. (Krüss, *B.* 21, 131).

Preparation.—Powdered *argyrodite* is heated to moderate redness with calcined Na_2CO_3 and flowers of S; the product is extracted with water, and exactly enough H_2SO_4Aq is added to decompose the Na_2S. After standing for a day the liquid is filtered, and HClAq is added so long as a pp. forms. The liquid is saturated with H_2S, and filtered; the pp. is washed with 90 p.c. alcohol saturated with H_2S. The sulphide of Ge thus obtained is roasted at a low temperature and warmed with HNO_3Aq. The oxide thus produced is strongly heated, and then reduced, either by heating in H, or by making into small balls with starch and water, and heating to bright redness between layers of charcoal, and then melting under borax (Winkler, *J. pr.* [2] 34, 177). For another method *v.* Winkler, *J. pr.* [2] 36, 177.

Properties.—Greyish-white, lustrous, very brittle; melts at c. 900°, and crystallises in regular octahedra on cooling. Only slightly volatilised by heating in H or N at 1350° (V. Meyer, *B.* 20, 497). Unchanged in air at ordinary temperature, but oxidised when heated in state of powder. Dissolved by H_2SO_4Aq but not by HClAq. The atom of Ge is tetravalent in the gaseous molecules $GeCl_4$ and GeI_4.

The at. w. has been determined by analysing $GeCl_4$, and determining the V.D., and hence mol. w. of the same compound, and also GeI_4 and GeS (Winkler, *J. pr.* [2] 34, 177). The value 72·3 is confirmed by measurements of the S.H. of Ge at 100°-400°. Lecocq de Boisbaudran has also calculated the at. w. from observations of the spectral lines of Ge (*C. R.* 102, 1291). The difference between the mean wave-lengths of the characteristic lines of Ge and Si is 443, and between Ge and Sn the difference is 624; this may be stated as 443 (1 + ·4051) = 624. In the cases of Ga and Al the difference is 149, and the difference between Ga and In is 205; this may be stated as 149 (1 + ·38584) = 205. The difference between the at. ws. of Ga and Al is 42·4, and the difference for Ga-In is 43·6; this may be stated as 42·4 (1 + ·028302) = 43·6. The difference between the at. ws. of Si and Sn is 90. From these data the number 72·31 is found for the at. w. of Ge, assuming that the relation between variation of at. ws. and wave-lengths in the three elements Si, Ge, Sn is the same as in the three elements Al, Ga, In (*v.* GALLIUM, *Chemical Relations of*, p. 598).

Germanium belongs to the same family as Si, Sn, and Pb; these four elements form the odd-series members of Group IV. Ge is both metallic and non-metallic in its chemical relations. The oxide GeO_2 dissolves in acids, but no salts have yet been isolated; this oxide also dissolves in KOH and K_2CO_3 when fused with these salts, and probably forms germanates analogous to the stannates; GeS_2 also dissolves in alkaline hydrosulphides probably forming thiogermanates. The existence of the two oxides and sulphides GeO and GeO_2, GeS and GeS_2; the composition and properties of $GeCl_4$, GeI_4, and GeF_4; the formation of liquid $GeHCl_3$ analogous to $SiHCl_3$ and $CHCl_3$, and of liquid $Ge(C_2H_5)_4$ similar to $Si(C_2H_5)_4$; and the isolation of H_2GeF_6 and salts of this acid; these mark the similarity between Ge and Si. Ge also appears to be capable of replacing Si in ultramarine.

Reactions.—1. Powdered Ge *heated in air* burns to GeO_2.—2. Oxidised to GeO_2 by *nitric acid*.—3. Dissolves in *sulphuric acid*, but not in *hydrochloric acid*.—4. Combines directly with *chlorine*, *bromine*, and *iodine*, to form GeX_4.—5. Heated in a current of *hydrogen chloride* $GeHCl_3$ is formed.—6. Heated with *mercuric chloride* or *bromide* $GeCl_4$ or $GeBr_4$ is produced.

Detection and Estimation.—The most characteristic reaction of Ge compounds is the production of white GeS_2 by saturating an alkaline solution with NH_4HS, and then adding excess of a mineral acid. In estimating Ge, excess of NH_4HS is added to an alkaline solution, a large excess of dilute H_2SO_4Aq is then added, and the liquid is saturated with H_2S; after standing 12 hours the ppd. GeS_2 is collected, and washed with dilute H_2SO_4Aq saturated with H_2S; the pp. is then washed off the filter, the residue on the filter is dissolved in ammonia, and this solution, together with the water used in washing off the pp., is evaporated to dryness in a weighed porcelain crucible, the main portion of the pp.

is now placed in the crucible, and the whole is evaporated to remove adhering H_2SO_4; the residue is heated, nitric acid is added, and the whole is again evaporated and heated strongly; the residue is now digested with ammonia (to remove H_2SO_4), then dried, heated strongly, and weighed as GeO_2. If the Ge is obtained as a thio salt, along with thio salts of Sb, As, and Sn, the solution is diluted to a definite volume, a measured portion is boiled with excess of normal H_2SO_4Aq, and the residual H_2SO_4 is determined volumetrically; the quantity of H_2SO_4 required to neutralise the solution is thus determined; the proper quantity of H_2SO_4 is then added to another measured portion of the liquid, and, after standing 12 hours, the liquid is filtered and evaporated to a small volume; NH_3Aq and NH_4HS are added, then excess of H_2SO_4Aq, and the Ge is ppd. as GeS_2 by saturating with H_2S (*v. supra*).

Germanium bromide $GeBr_4$. A strongly fuming colourless liquid, which solidifies a little below 0° to white crystals; decomposed by water with ppn. of GeO_2 and production of much heat. Formed by heating Ge in Br, or with $HgBr_2$ (Winkler, *J. pr.* [2] 36, 177).

Germanium chloride $GeCl_4$. Mol. w. 213·78. (86°). V.D. 107·5 at 200° to c. 650° (Nilson a. Pettersson, *Z. P. C.* 1, 27). S.G. $\frac{18°}{18°}$ 1·887. Critical temp. = 276·9° (N. a. P.) (vapour-pressures, *v.* N. a. P., *l.c.*). A thin colourless liquid, fuming in air; decomposed by water to GeO_2; partially reduced to Ge by heating in H. Formed by heating Ge in Cl, shaking the product with Hg and distilling; or by heating powdered Ge with 8 times its weight of $HgCl_2$ (W., *J. pr.* [2] 34, 177).

When HCl is passed over heated GeS, a chloride lower than $GeCl_4$ is probably obtained.

Germanium chloroform $GeHCl_3$. Mol. w. 179·41. V.D. at 178° 80·3. A thin colourless liquid, boiling at 72°: formed by gently heating Ge in dry HCl, and separating the heavier liquid from the lighter (separation of the distillate into two layers takes place slowly) (W., *J. pr.* [2] 36, 177).

Germanium ethide $Ge(C_2H_5)_4$. Mol. w. 188·06. V.D. 123. A colourless liquid of slightly alliaceous odour; boiling at 160°. Prepared by mixing $ZnEt_4$ with $GeCl_4$, and keeping the mixture cold, as the reaction occurs violently. Slightly lighter than, and immiscible with, water. Unchanged by mixture with oxygen at ordinary temperatures. Burns in air to GeO_2 (W., *l.c.*).

Germanium fluorhydric acid H_2GeF_6Aq. When vapour of GeF_4 (obtained by strongly heating $GeF_4.3H_2O$) is led into water, the solution contains the acid H_2GeF_6 (W., *l.c.*).

POTASSIUM GERMANIO-FLUORIDE K_2GeF_6 (W., *l.c.*; also Krüss a. Nilson, *B.* 20, 1696). Obtained by adding KHF_2 to a solution of GeO_2 in HFAq (N. a. P.), or by using KCl instead of KHF_2 (W.), allowing the pp. to settle, filtering, and drying at dull red heat. According to N. a. P. the salt is melted without loss of weight at bright redness; and according to W. the salt loses weight above a red heat. Not hygroscopic. S. at 100° = 2·6 (N. a. P.). Crystallises in hexagonal forms; $a:c = 1:·80389$; isomorphous with $(NH_4)_2SiF_6$ (N. a. P.).

Germanium fluoride $GeF_4.3H_2O$. Very deliquescent crystals, obtained by dissolving GeO_2 in conc. HFAq, and evaporating over H_2SO_4. When heated, HF and H_2O are evolved, and some GeO_2 is formed; heated to redness GeF_4 is evolved, and about half the Ge remains as GeO_2. Pure GeF_4 has not yet been obtained; Winkler (*J. pr.* [2] 36, 177) tried to prepare it, (1) by the action of H on heated K_2GeF_6; (2) by heating $GeF_4.3H_2O$ in dry CO_2; (3) by heating together GeO_2, CaF_2, and H_2SO_4; (4) heating a mixture of K_2GeF_6 with H_2SO_4. GeF_4 is doubtless a solid capable of being volatilised (W.).

Germanium iodide GeI_4. Mol. w. 578·42. [144°]. (350°–400°) (W., *J. pr.* [2] 34, 177). V.D. at 440° 272·5 (Nilson a. Pettersson, *Z. P. C.* 1, 36). Dissociation, probably into GeI_2 and I, begins c. 650°. A yellow, very hygroscopic solid, vapour is inflammable; mixed with air and ignited, detonates feebly. Produced by heating Ge in a current of CO_2 containing I vapour.

Germanium oxides. GeO has probably been isolated. GeO_2 is a well-marked body.

GERMANIC OXIDE GeO_2. Produced by burning Ge in O; or by oxidising Ge by HNO_3; or preferably by decomposing $GeCl_4$ by water. Dense white gritty solid; S.G. $\frac{18°}{18°}$ 4·703. S. at 20° = ·4; at 100° = 1·05 (W., *J. pr.* [2] 34, 177). Separates from solution in water as microscopic rhombic crystals. Aqueous solution has a sour taste. GeO_2 dissolves readily in fused KOH and K_2CO_3. Probably forms salts with acids, but none has yet been isolated.

GERMANIOUS OXIDE GeO. Described by Winkler as obtained by boiling $GeCl_2$ with KOHAq, and heating the hydroxide (probably GeO_2H_2) thus formed in CO_2; but there are doubts as to the isolation of $GeCl_2$, inasmuch as the substance formerly supposed to be this chloride has been shown to be $GeHCl_3$ (W., *J. pr.* [2] 36, 177). GeO is also formed in small quantity when powdered Ge is melted under borax. GeO is described as a greyish-black solid; e. sol. HClAq, forming a solution which reduces $KMnO_4Aq$ to K_2MnO_4Aq and ppts. Au and Hg from their salts.

Germanium oxychloride (?) $GeOCl_2$. When Ge is heated in dry HCl, two liquids of almost the same S.G. are obtained. The distillate slowly separates into two layers; the lighter is an oxychloride, probably $GeOCl_2$. Winkler (*J. pr.* [2] 36, 177) describes it as a colourless, oily, non-fuming liquid, which adheres to glass, and boils much above 100°, seemingly without decomposition.

Germanium, salts of. GeO_2 probably forms salts by dissolving in acids, but none has yet been isolated.

Germanium sulphides. Both GeS and GeS_2 have been isolated.

GERMANIC SULPHIDE GeS_2. Obtained by adding NH_4HS to an alkaline solution of GeO_2, then adding considerable excess of H_2SO_4Aq, saturating with H_2S, washing first with H_2SO_4Aq saturated with H_2S and then with alcohol, and drying *in vacuo*. A white powder. Heated in dry CO_2 it is partly volatilised, and apparently also partially decomposed. If GeS_2 is washed with water until free from acid, and then suspended in water, an emulsion is formed which requires several weeks to clear. About 1 part of the sulphide treated thus dissolves in 229·1 parts water; the solution is feebly acid to litmus; it soon decomposes with evolution of H_2S. GeS_2 dissolves easily in alkaline hydrosulphides, probably with formation of thiogermanates.

Germanious sulphide GeS. Mol. w. 104·28. V.D. 1100°-1500° = 48 (Nilson a. Pettersson, *Z. P. C.* 1, 37). Greyish-black plates; very lustrous; red by transmitted light. Obtained by heating GeS_2 in a slow current of H. Heated in air gives GeO_2. Dissolves easily in warm KOHAq, giving residue of Ge; addition of H_2S to this solution ppts. GeS as a reddish-brown amorphous solid. M. M. P. M.

GINGEROL. An alkaline substance said to occur in ginger, the root of *Zingiber officinalis* (Thresh, *Ph.* [3] 12, 721). According to Thresh, the ethereal extract contains, besides gingerol, three resins $C_{16}H_{24}O_3$, $C_{46}H_{54}O_{10}$, and $C_{43}H_{60}O_8$, and a terpene. By extracting ginger with alcohol, and distilling the extract with steam, Stenhouse and Groves (*C. J.* 31, 553; *cf.* Papousek, *A.* 84, 352) obtained a light essential oil which yielded protocatechuic acid on fusion with soda.

GINGKOIC ACID $C_{24}H_{48}O_2$. [35°]. Occurs in the fruit of *Gingko biloba* (Schwarzenbach, *J.* 1857, 529; *Vicrt. pr. Pharm.* 6, 424).

GLASS. A mixture of K or Na silicate, or of ooth, with one or more silicates insol. water, such as silicate of Al, Ba, Ca, Fe, Pb, Mn, Mg, or Sr. Pure silicate of K or Na is acted on by water; silicate of Ca is decomposed by acids; but a mixture of the two is only very slowly acted on by water or the commoner acids. The greater the proportion of silica and alumina in the glass, the less fusible is it, and the more slowly is it acted on by acids.

Glass is slowly acted on by hot water; the more readily the greater the proportion of soda or potash in the glass. Glass is corroded or etched by HFAq with formation of gaseous SiF_4. Glasses poor in silica are acted on by most acids, which dissolve out bases and separate silica. Potash or soda dissolves out silica from glass, especially when the solutions are hot and concentrated. Lead glass is blackened by heating owing to reduction of some of the Pb silicate to Pb. For details regarding different kinds of glass, *v.* Dictionary of technical chemistry. M. M. P. M.

GLAUCINE. An alkaloid obtained by Probst (*A.* 31, 241) from the leaves of the yellow horned poppy (*Glaucium flavum*) growing on sandy seashores. Colourless crusts of nacreous scales (from water). It is ppd. from solutions of its salts by NH_3 as a curdy mass which after some time becomes pitchy. It is m. sol. hot water, v. sol. alcohol and ether. Tastes bitter. Its solution is alkaline in reaction. Hot H_2SO_4 gives a violet colour; on adding water a red solution is formed, whence NH_3 throws down an indigo-blue pp. The hydrochloride, sulphate, and phosphate of glaucine are crystalline, and v. sol. water and alcohol, insol. ether.

GLAUCOMELANIC ACID *v.* Ellagic acid.

GLAUCOPICRINE. An alkaloid contained in the roots of *Glaucium flavum* (*sive luteum*) (Probst, *A.* 31, 254). Granular crystals, sol. water and alcohol, sl. sol. ether. Its salts have an extremely bitter and nauseous taste. Animal charcoal removes glaucopicrine from solutions of its salts. Hot conc. H_2SO_4 gives a dark green pitchy product, insol. water, acids, and ammonia. The hydrochloride crystallises in rhomboidal plates or in bundles of prisms, sol. water, insol. ether. The sulphate and phosphate are also crystallisable.

GLIADIN *v.* Proteïds.

GLOBIN *v.* Hæmoglobin and Proteïds.

GLOBULARIN $C_{15}H_{20}O_8$. Occurs in the leaves of *Globularia Alypum* (Walz, *N. J. P.* 13, 281; Heckel, *A. Ch.* [5] 28, 72; *C. R.* 95, 90). Amorphous; sol. water, alcohol, and ether. Tastes bitter. Acid in reaction. Ppd. from its aqueous solution by iodine and by tannin. Resolved by boiling dilute acids into glucose and globularetin C_9H_6O. Globularetin is converted into cinnamic acid by boiling KOHAq.

GLOBULIN *v.* Proteïds.

GLOBULOSE *v.* Proteïds.

GLUCIC ACID $C_{12}H_{22}O_{12}aq.$ (R.); $C_{16}H_{24}O_{13}$ (M.). *Glycic acid.*

Formation.—1. A solution of glucose is saturated with lime or baryta and left for several weeks. On adding lead subacetate a bulky pp. of lead glucate is formed (Peligot, *A. Ch.* 67, 154).—2. Glucose melted at 100° in its water of crystallisation is mixed with warm conc. KOHAq; as soon as the first reaction has ceased the liquid is diluted and the glucic acid ppd. by lead subacetate (Persoz).—3. Cane-sugar is boiled with dilute H_2SO_4 in contact with the air. The product is filtered, neutralised by $CaCO_3$, evaporated to dryness, dissolved in a little water, and mixed with alcohol which ppts. calcium apoglucate while acid calcium glucate remains in solution (Mulder, *A.* 36, 243).

Properties.—Amorphous mass, v. sol. water and alcohol. Turns brown at 100°. The aqueous solution turns brown when boiled in contact with the air or with dilute H_2SO_4 or HClAq, apoglucic acid being among the products. According to Grote and Tollens (*A.* 175, 181) the calcium glucate of Mulder is calcium levulate $C_5H_8CaO_3$.

Salts.—(Reichardt, *Vierteljahr. pr. Pharm.* 19, 384, 503.)—$Na_6H_6A'''_4$: [100°]; hygroscopic. —$CaH_4A'''_2aq.$—$Ba_3H_3A'''_2 3aq.$ — $BaH_4A'''_2aq$: very hygroscopic.—$MgHA'''_2aq.$ — AlA''': yellowish-white mass. — $Fe_3H_3A'''_2 3aq.$ — $Pb_3C_{12}H_{16}O_{12}$ (at 150°).

Apoglucic acid $C_{18}H_{22}O_{11}$ (dried at 100°)? Formed by boiling glucic acid with water or dilute acids or cane-sugar with dilute H_2SO_4 (Mulder). Amorphous brown mass, v. sol. water, sl. sol. alcohol, insol. ether. Its alkaline salts form deep red solutions.—$PbC_{18}H_{16}O_9$.—$Ag_2C_{18}H_{18}O_{10}$: brown.—$CaC_{18}H_{18}O_{10}$ (at 130°): brown amorphous mass.

Isoapoglucic acid. Formed by heating acetone with chlorine, potash, and HCl successively (Mulder, *Z.* 1868, 51).—$PbCH_2O_4$.

GLUCINUM *v.* Beryllium.

GLUCO-COUMARIC ALDEHYDE *v.* *Glucoside* of Coumaric aldehyde.

GLUCODRUPOSE $C_{24}H_{36}O_{16}$. The chief constituent of concretions in pears (Erdmann, *A.* 138, 1). Pale yellowish grains. Insol. ordinary solvents, alkalis, cold dilute acids, and

Schweizer's solution. Split up by boiling dilute acids into glucose and drupose $C_{12}H_{20}O_8$.

GLUCOFERULIC ALDEHYDE *v.* Ferulic aldehyde.

GLUCOLIGNOSE $C_{30}H_{46}O_{21}$? Occurs in pine wood (Erdmann, *A. Suppl.* 5, 223). Yellowish solid, insol. ordinary solvents, v. sl. sol. Schweizer's solution. Split up by boiling dilute HCl into glucose and lignose $C_{18}H_{26}O_{11}$? (*v.* Cellulose).

GLUCONIC ACID $C_6H_{12}O_7$ *i.e.* $CH_2(OH).(CH.OH)_4.CO_2H$. $[\alpha]_D = 5{\cdot}8°$.

Formation.—1. From glucose, cane-sugar, maltose, starch, soluble starch, and dextrin by successive treatment with bromine (or chlorine) and Ag_2O (Hlasiwetz a. Habermann, *A.* 155, 120; Habermann, *B.* 5, 167; *A.* 162, 297; 172, 11; Reichardt, *B.* 8, 1020; Kiliani, *A.* 205, 182; Herzfeld, *A.* 220, 342).—2. By oxidising glucose with red mercuric oxide and baryta-water (Herzfeld, *A.* 245, 32).—3. By the fermentation of glucose by mycoderma aceti in presence of $CaCO_3$ and an infusion of yeast (Boutroux, *J. Th.* 1880, 52).

Preparation.—1. Dextrin (30 g.) is heated in a closed vessel with bromine (60 g.) and water (500 c.c.) for 6 hours at 100°. The product is neutralised with Ag_2O, filtered, freed from silver by H_2S, and evaporated over the water-bath (Herzfeld, *A.* 220, 342).—2. An aqueous solution of cane-sugar is treated with bromine until the Br ceases to disappear. The HBr formed is removed by PbO, the solution is then ppd. by H_2S, and the filtrate after concentration saturated with $ZnCO_3$. The zinc-salt is subsequently decomposed by H_2S (Grieshammer, *Ar. Ph.* [3] 15, 193).

Properties.—Uncrystallisable syrup (containing 2aq); loses aq at 100°, and the second aq at 125°. Sol. water, insol. alcohol. Does not reduce Fehling's solution. Decomposed by alkaline hydroxides, alkaline carbonates, baryta, and lime.

Reactions.—1. Reduced by HI and phosphorus to the lactone of oxy-*n*-hexoic acid (Kiliani a. Kleemann, *B.* 17, 1296).—2. Protracted treatment with *bromine* forms bromoform, bromo-acetic acid, and oxalic acid.—3. Ag_2O forms glycollic acid.—4. HNO_3 (S.G. 1·4) oxidises it to saccharic and oxalic acids.

Salts.—Ammonium salt: crystalline (Boutroux, *C. R.* 91, 236; 104, 369). CaA'_2aq (from dilute alcohol). $[\alpha]_D = 5{\cdot}9$. S. (of CaA'_2) 3·8 at 16·5°.—$CaA'_2 2aq$: groups of slender needles.—$CaC_6H_{10}O_7 x aq$.—$BaA'_2 3aq$: prisms. S. (of BaA'_2) 3·3 at 15·5°.—$BaA'_2 2aq$.—$BaA'_2 aq$.—$BaC_6H_{10}O_7 x aq$.—$ZnA'_2 5aq$.—CdA'_2.—PbA'_2.—$Pb_2C_6H_8O_7$ (at 120°).

Ethyl ether EtA'. Obtained in combination with $CaCl_2$ as $(EtA')_2CaCl_2$ by passing HCl into an alcoholic solution of the calcium salt. The free ether crystallises in needles.

Penta-acetyl derivative of the ethyl ether $C_5H_6(OAc)_5.CO_2Et$. [102°] (Herzfeld, *A.* 245, 32).

Para-gluconic acid $C_6H_{12}O_7$.

Preparation.—If gluconic acid is left in contact with nitric acid (S.G. 1·3) for some time, and the solution neutralised with alkaline carbonates, salts of an isomeric paragluconic acid are obtained, and can be separated from the metallic nitrate by alcohol. The free acid is a colourless syrup, of strong acid reaction, sol. water, insol. alcohol (Hönig, *M.* 1, 48). The alkaline earth salts of this acid cannot be obtained in a crystalline form, thus differing from those of gluconic acid. According to Volpert (*B.* 19, 2621) it is identical with gluconic acid.

Salts.—KA' (at 100°): crystalline leaflets.—NH_4A' (at 100°): colourless monoclinic needles.—$Pb_2C_6H_8O_7$: voluminous white pp.

GLUCO-PROTEÏNS *v.* Proteïds.

GLUCOSAMINE *v.* Proteïds; *Appendix C.*

GLUCOSAN *v.* Sugars.

GLUCOSE *v.* Sugars.

GLUCOSIDES. Substances which, when decomposed by dilute acids, yield glucose (or some other sugar) and another substance not belonging to the class of carbohydrates (Laurent, *A. Ch.* [3] 36, 330). They are for the most part natural products occurring in plants. They may be viewed as compound ethers containing the group $(C_6H_{11}O_5)$, which is turned out on hydrolysis $RC_6H_{11}O_5 + H_2O = RH + C_6H_{12}O_6$. Some glucosides may be obtained artificially by the use of acetochlorhydrose $C_6H_7ClAc_4O_5$: thus helicin is formed by the action of this body upon potassium salicylic aldehyde (Michael, *Am.* 1, 308). Inasmuch as many sugars may be converted into glucose by boiling with dilute acids, the appearance of glucose after this operation does not necessarily involve the pre-existence of the residue of that particular sugar in the glucoside. The hydrolysis may be effected by boiling with dilute HCl, dilute H_2SO_4, baryta-water, or dilute alkalis. Some nitrogenous ferments, frequently existing in the plants themselves, can effect the hydrolysis even in the cold; *e.g.* emulsin in almonds, myrosin in mustard, and erythrozym in madder. The glucosides are solid, soluble in water, and usually crystalline. They give Pettenkofer's reaction with bile salts and H_2SO_4. The following are among the more important glucosides that yield glucose when boiled with dilute acids: arbutin, ruberythrin, salicin, daphnin, æsculin, jalapin, helleborin, turpethin, populin, bryonin, ononin, and the nitrogenous glucosides amygdalin, solanin, indican, and chitin. The following phloroglucides resemble glucosides but yield phloroglucin instead of glucose on hydrolysis: phloretin, quercetin, and madurin. The following 'phloroglucosides' yield both phloroglucin and a sugar: phlorizin, quercitrin, robinin, and rutin.

(α)-**GLUCOSINE** $C_6H_8N_2$. (136°). S.G. $\frac{0}{}$ 1·038. V.D. 3·81. A body formed by heating aqueous ammonia with glucose at 100° (Tanret, *Bl.* [2] 44, 102). Limpid volatile liquid. Inactive to light.—B'HCl: very deliquescent crystals.—B'EtI: pearly crystals.

(β)-**Glucosine** $C_6H_8N_2$. (160°). S.G. $\frac{0}{}$ 1·012. V.D. 3·87. Formed by the action of ammonia on glucose at the same time as its isomeride (Tanret, *Bl.* [2] 44, 104). Liquid. The platinochlorides of the two glucosines are partially decomposed by boiling water (O. de Coninck, *Bl.* [2] 45, 131).

GLUTACONIC ACID $CO_2H.CH_2.CH{:}CH.CO_2H$. [132°]. (Isomeric with citraconic acid.) From di-carboxy-glutaconic ether (*q.v.*) and boiling HCl (Conrad a. Guthzeit, *A.* 222, 253). White prisms. V. sol. water, alcohol, and ether. Not decomposed below 180°. Gives no colour with $FeCl_3$. Sodium amalgam reduces it to glutaric acid.

Salts.—ZnA''.—Ag_2A'.

Reference.—Chloro-glutaconic acid.

GLUTAMIC ACID $C_5H_9NO_4$ *i.e.* $C_3H_5(NH_2)(CO_2H)_2$. [202°]. S. 1 at 15°; S. (80 p.c. alcohol) ·07 at 15°. Occurs, probably as its amide, in pumpkin seeds (Schulze a. Barbieri, *B.* 11, 710, 1233), vetch seeds (Gorup-Besanez, *B.* 10, 780) and beet-root juice (Scheibler, *B.* 2, 296; Schulze, *B.* 10, 85; 16, 312). It may be isolated from molasses after the sugar has been removed by the strontium process (Scheibler, *B.* 17, 1725). Formed, together with aspartic acid, by boiling vegetable proteïds with dilute H_2SO_4 (Ritthausen, *J. pr.* 99, 454; 107, 218). Formed also by boiling caseïn with HCl and $SnCl_2$ (Hlasiwetz a. Habermann, *A.* 169, 157). Among the products of the decomposition of proteïds by baryta Schützenberger (*A. Ch.* [5] 16, 375) found an acid $C_5H_9NO_4$ [150°] which formed two silver salts $AgHA''$ and Ag_2A'', apparently not to be identified with glutamic acid.

Preparation.—The portion of wheat gluten that is soluble in alcohol (mucelin) is boiled for 20 hours with H_2SO_4 (2½ pts.) diluted with water (6½ pts.); the product is neutralised by lime; excess of lime is removed by oxalic acid; excess of oxalic acid by lead carbonate; and excess of lead by H_2S. The strongly acid liquid yields by evaporation a crystalline mixture of tyrosine, leucine, and glutamic acid, from which, by treatment with hot water (which leaves the tyrosine undissolved), and then with alcohol of 30 p.c. (which chiefly dissolves the leucine), and recrystallisation from water with addition of animal charcoal, and from alcohol of 30 p.c., the glutamic acid is obtained pure.

Properties. — Trimetric tetrahedra; $a{:}b{:}c = ·801{:}1{:}1·179$ (Von Rath); $= ·687{:}·855{:}1$ (Oebbeke). Sl. sol. cold water, insol. alcohol. Its solutions are acid, and have an astringent taste. In aqueous solution it is dextrorotatory, $[\alpha]_D = 10·2$ in a 2 p.c. solution at 21°. A solution of its hydrochloride B'HCl is also dextrorotatory, $[\alpha]_D = 20°$ in a 4 p.c. solution at 21°; but its neutral salts are lævorotatory, thus for CaA'' $[\alpha]_D = -3·7°$ in a 5 p.c. solution at 22°. Its solution is not ppd. by lead acetate even on addition of ammonia. Glutamic acid does not reduce Fehling's solution. On distillation it gives pyroglutamic acid $C_5H_7NO_3$, and afterwards pyrrole.

Reactions.—1. *Nitrous acid* converts it into an inactive oxy-glutaric acid.—2. *Baryta-water* at 155° renders it inactive; but when some *Penicillium glaucum* is placed in a solution of the inactive glutamic acid it again becomes active (Schulze a. Bosshard, *B.* 18, 388). The inactive acid is m. sol. water (S. 1·7 at 17°).

Salts.—The glutamates of the alkalis and alkaline earths are v. sol. water and alcohol, and dry up to gummy masses; the copper salt is characteristic and very sparingly soluble.—$HNaA''$.—$(NH_4)_2A''$.—NH_4HA''.—$BaH_2A''_2$.—$BaA''6aq$: groups of needles.—$CuA''2\frac{1}{2}aq$: S. ·03 in the cold; ·25 at 100° (Hofmeister, *Sitz. W.* 75, 469).—$CuA''2aq$: blue crystalline powder (Schulze a. Bosshard, *B.* 16, 313).—$CuA''3aq$.—Ag_2A'' (at 100°).—$H_2A''HCl$ (at 100°): triclinic tables; sl. sol. conc. HClAq.—$H_2A''HBr$.

Mono-ethyl ether $EtHA''$. [165°]. Crystalline, v. sol. water, sl. sol. cold alcohol, insol. ether. Alcoholic ammonia at 150° converts it into glutimide.

Amide $C_5H_{10}N_2O_3$ *i.e.* $C_3H_5(NH_2)(CO_2H)(CO.NH_2)$. S. 4 at 16°. Occurs in the juice of red beet-root, from which it is isolated by precipitation with $Hg(NO_3)_2$ (Schulze a. Bosshard, *B.* 16, 312). Occurs also in pumpkin-seeds (Schulze a. Barbieri, *J. pr.* [2] 20, 388; 32, 457). Slender white needles; v. sol. hot water; insol. absolute alcohol. Its aqueous solution is inactive, but its solution in dilute H_2SO_4 or oxalic acid is dextrorotatory. Heated with acids or alkalis it gives glutamic acid.

Imide $C_3H_5(NH_2)\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH$. Formed by heating ammonium glutamate for five hours at 190°. Needles. S. 8·7 at 15·5°.—$C_5H_8N_2O_2HCl$.—$C_5H_7AgN_2O_2$.

GLUTANIC ACID *v.* Oxy-glutaric acid.

GLUTARIC ACID $C_5H_8O_4$ *i.e.* $CO_2H.CH_2.CH_2.CH_2.CO_2H$. *Normal pyrotartaric acid. Deoxyglutanic acid.* Mol. w. 132. [98°]. (c. 300°). S. 83 at 14°. S.H. (0°–94°) ·3461 (Hess, *W.* [2] 35, 410). Occurs as the K salt in the grease of sheep's wool (Buisine, *C. R.* 107, 789).

Formation.—1. By heating oxy-glutaric acid (1 pt.) with conc. HIAq (4 pts.) at 120° for 8 hours (Dittmar, *J. pr.* [2] 5, 338).—2. By the saponification of trimethylene cyanide prepared from trimethylene bromide and alcoholic KCy (Lermontoff, *B.* 9, 1441; Reboul, *Bl.* [2] 25, 386; Markownikoff, *A.* 182, 341).—3. From α-acetyl-glutaric ether (*q. v.*) and conc. alcoholic KOH (Wislicenus a. Limpach, *A.* 192, 128).—4. By heating menthol with HNO_3 (20 vols.) (Moriya, *C. J.* 39, 78).—5. By treating glutaconic acid with sodium amalgam (Conrad a. Guthzeit, *A.* 222, 254).—6. By heating propane tetracarboxylic acid to 180° (Kleber, *A.* 246, 110).—7. By boiling di-oxy-propane tri-carboxylic acid with HIAq and phosphorus (Kiliani, *B.* 18, 640). 8. Among the products of the oxidation of myristic acid by HNO_3 (Noerdlinger, *B.* 19, 1898).

Properties.—Large transparent monoclinic prisms. V. e. sol. water, alcohol and ether. When heated with bromine and water at 120° some di-bromo-succinic acid is formed (E. Bourgoin a. Reboul, *C. R.* 84, 556).

Salts.—NH_4HA'': concentric crystals.—$(NH_4)_2A''$.—$NaHA''2aq$.—$Na_2A''xaq$.—KHA''.—$K_2A''aq$.—$CaA''4aq$: stellate groups of slender needles, more sol. cold than hot water. S. 60 at 16°.—$BaA''5aq$: small transparent needles, v. sol. water.—$MgA''3aq$: small needles (from dilute alcohol); v. e. sol. water.—ZnA'': needles. S. ·1 at 18°. The solution deposits on heating characteristic minute rectangular plates with re-entering angles.—$PbA''aq$: heavy crystalline pp.—$CuA''\frac{1}{2}aq$.—Ag_2A'': needles (from hot water).

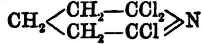
Mono-ethyl ether $EtHA''$. An oil formed by the action of alcohol on the anhydride in the cold (M.).

Di-ethyl ether Et_2A''. (237°). S.G. 1·025.

Chloride $C_3H_6(COCl)_2$. (217°) (Reboul, *A. Ch.* [5] 14, 510).

Anhydride $C_3H_6(C_2O_3)$. [57°]. (c. 287°). From the silver salt and AcCl(M.). Slender needles.

Imide $C_5H_7NO_2$. [152°]. Prepared by heating at 175°–180° the mixture of neutral and acid ammonium glutarates, obtained by neutralising glutaric acid with ammonia. Ammonia and water are given off, and the imide collects partly in the neck, partly at the bottom of the flask. The product is obtained in the pure state by crystallising from alcohol. Brilliant scales, subliming above its melting-point, sol. water and benzene, insol. ether. Its **silver salt** is a crystalline powder. Heated with zinc-dust it forms a hydrocarbon and a basic substance, probably a hydride of pyridine. After heating with PCl_5 at 60° on distilling the residue in a current of steam, a substance $C_5H_6Cl_3N$ is obtained, crystallising in needles [60°] which appears to possess the constitution



$$CH_2\begin{matrix}\diagup CH_2—CCl_2 \diagdown \\ \diagdown CH_2—CCl \diagup\!\!\diagup\end{matrix}N$$

, inasmuch as, when heated with hydriodic acid and amorphous phosphorus, it yields a substance approximately of the composition of chloropyridine (Bernheimer, *G.* 12, 281).

GLUTAZINE *v.* Di-oxy-amido-pyridine.

GLUTEN *v.* Proteïds.

GLUTEN-FIBRIN *v.* Proteïds.

GLUTIC ACID *v.* Glutinic acid.

GLUTIMIC ACID $C_5H_7NO_3$. [180°]. One of the products of the decomposition of proteïds with barium hydroxide; glistening, voluminous prisms, sparingly sol. cold water, insol. cold alcohol. A monobasic acid, forming a sparingly soluble mercuric salt (Schützenberger, *A. Ch.* [5] 16, 373).

GLUTIN *v.* Proteïds.

GLUTINIC ACID $C_5H_4O_4$ *i.e.* $HO_2C.C\vdots C.CH_2.CO_2H$. [146°]. Formed by the action of alcoholic KOH upon β-chloro-glutaconic acid $HO_2C.CH:CCl.CH_2.CO_2H$; the yield is 30-40 p.c. of the theoretical. Slender needles, v. sol. alcohol and ether, insol. benzene and chloroform. On heating the acid or its monopotassium salt with water, it is converted with evolution of CO_2 into a very unstable monobasic acid, probably $HC\vdots C.CH_2.CO_2H$, which gives the acetylene reactions.—$A''Pb$: white pp. —$^xA''K_2xaq$: long flat needles.—$^xA''Ba\,xaq$: slender needles (Burton a. Pechmann, *B.* 20, 148).

GLYCERAMINE *v.* Glycidamine.

GLYCERIC ACID $C_3H_6O_4$ *i.e.* $CH_2(OH).CH(OH).CO_2H$. Mol. w. 106. *αβ-Di-oxy-propionic acid. Heat of neutralisation* by $\frac{1}{2}Na_2O = 11{,}334$; by $Na_2O = 12{,}127$ (Gal a. Werner, *Bl.* [2] 47, 163).

Formation.—1. By the gradual oxidation of glycerin by nitric acid (Debus, *P. M.* [4] 15, 195; *A.* 109, 227; Socoloff, *A.* 106, 95).—2. By the spontaneous decomposition of nitroglycerin (De la Rue a. Müller, *A.* 109, 122).—3. By heating glycerin (1 mol.) with bromine (2 mols.) and a large quantity of water at 100° (Barth, *A.* 124, 341).—4. By heating α-chloro-β-oxy-propionic acid or β-chloro-α-oxy-propionic acid with moist Ag_2O (Melikoff, *C. C.* 1881, 364; *B.* 13, 272; Frank, *A.* 206, 348).—5. By heating αβ-di-bromo-propionic acid with moist Ag_2O (Beckurts a. Otto, *B.* 18, 238).—6. By heating oxy-acrylic acid $C_3H_4O_3$ with water (Melikoff).

Preparation.—1. By mixing 50 g. of glycerin with 50 g. of water in a large glass tube, and adding, by means of a funnel reaching to the bottom, 50 g. of fuming nitric acid. After three or four days the contents of three such tubes are slowly evaporated on the water-bath down to about 270 g., and the syrupy mass thus obtained is preserved in a flask allowing the escape of gas, which is slowly given off. 1,620 g. of the syrupy mass are next mixed with 11 litres of water, 2,400 g. of white lead are gradually added, and the mixture is left to stand for a day. The vessel is then warmed, with constant stirring, to 61°-65°, and kept at this temperature for two hours. The liquid is decanted and allowed to deposit crystals, the mother-liquor added to the solid mass, the water lost by evaporation replaced, and the operation repeated two or three times. The lead salt thus obtained is decomposed by H_2S (Mulder, *B.* 9, 1902; *cf.* Beilstein, *A.* 120, 226).—2. Mercuric oxide and baryta are added to a concentrated boiling aqueous solution of glycerin. When the liquid is saturated with baryta the addition of HgO is continued until reduction no longer takes place. The liquid is filtered, treated with CO_2, again filtered, and evaporated to a syrup, which is freed from glycerin by washing with alcohol. The residue is dissolved in water, the Ba is ppd. by the calculated quantity of H_2SO_4, and the glyceric acid which remains purified, if necessary, by means of its calcium salt. The yield is 45 p.c. of the glycerin used (Börnstein, *B.* 18, 3357).

Properties.—Uncrystallisable syrup; miscible with water and alcohol, insol. ether. When heated for some time at 105° it is converted into a soft, very tenacious, **anhydride** $C_3H_4O_3$; further application of heat gives formic, acetic, pyruvic, and pyrotartaric acids and an acid $C_6H_{10}O_6$ [83°] (Moldenhauer, *A.* 131, 323; Böttinger, *A.* 196, 92). Distillation with $KHSO_4$ forms pyruvic acid (Erlenmeyer, *B.* 14, 321). Glyceric acid prevents the ppn. of cupric and ferric hydrates by potash. It is optically inactive, but a solution of ammonium glycerate is rendered lævorotatory by *Penicillium glaucum* (Lewkowitsch, *B.* 16, 2720).

Reactions.—1. *Iodide of phosphorus* forms β-iodo-propionic acid.—2. Boiling conc. KOHAq forms oxalic and lactic acids.—3. *Potash-fusion* gives formic and acetic acids.—4. PCl_5 gives $CH_2Cl.CHCl.COCl$ (Wichelhaus, *A.* 135, 248).

Salts.—NH_4A': radiating deliquescent crystals.—KHA'_2: small crystals; the neutral K salt decomposes on evaporation.—$CaA'_2\,2aq$: nodules composed of minute tables or prisms; sol. water, insol. alcohol; on adding alcohol to its aqueous solution monoclinic crystals are got.—SrA'_2: crystals; nearly insol. cold, v. sol. hot, water (Garzarolli-Thurnlack, *A.* 182, 190).—BaA'_2. large spherical aggregates of concentric laminæ, v. e. sol. hot water, insol. alcohol.—$MgA'_2\,3aq$: stellate groups of small efflorescent crystals.—ZnA'_2aq: small crystals.—$CdA'_2\,2aq$.—PbA'_2.—CuA'_2: minute sky-blue crystals, m. sol. cold water.—$MnA'_2\,3aq$.—AgA': minute prisms (from water).

Ethyl ether EtA'. (230°-240°). S.G. $\frac{0}{0}$

1·193. Formed by heating glyceric acid (1 pt.) with alcohol (4 pts.) at 175° (Henry, *B.* 4, 701). Sticky liquid. A mixture of HNO_3 and H_2SO_4 converts it into its oily di-nitrate $C_3H_3(NO_3)_2OEt$.

Anhydride or *lactone* $C_3H_4O_3$. Separates from an aqueous solution of glyceric acid evaporated at 100° and left to rest. Slender six-sided needles (from water). Insol. alcohol and ether. It dissolves in 647 pts. of boiling water, by which it is slowly re-converted into glyceric acid.

GLYCERIC ALDEHYDE (?) $C_3H_6O_3$ or $^{\times}C_6H_{12}O_6$.

Preparation.—By the action of platinum black (best prepared by the method of Idrawkowitsch) on glycerin mixed with double its weight of water. The mass is extracted with water, and concentrated on a water bath *in vacuo*.

Reactions.—Reduces Fehling's solution and ammoniacal nitrate of silver. Is coloured yellow on boiling with lime or baryta water. Becomes strongly heated when shaken with a solution of $NaHSO_3$, after which alcohol ppts. a gummy matter, but Na_2CO_3 or H_2SO_4 do not set free an aldehyde from this mass. Phenyl-hydrazine hydrochloride and NaOAc gives a coloured pp.; on fractional ppn. several derivatives are obtained, none of which have been obtained pure. Of the part soluble in alkalis after a crystallisation from benzene, and one from weak alcohol, the melting-point is constant [193°]. The aldehyde ferments with yeast, but the quantity of CO_2 obtained is small compared to its reducing power (Grimaux, *Bl.* [2] 47, 885; *cf.* Renard, *C. R.* 82, 562). The same body occurs among the products of the action of nitric acid upon yeast, and it appears to be closely allied to the sugars (Grimaux, *C. R.* 105, 1175).

GLYCERIN $C_3H_8O_3$ *i.e.* $CH_2OH.CH(OH).CH_2OH$. *Glycerine. Glycerol.* Mol. w. 92. [20°] (Nitsche, *D. P. J.* 209, 145). (290° cor.). S.G. $\frac{20}{20}$ 1·2635 (Nicol, *Ph.* [3] 18, 302); $\frac{15}{15}$ 1·2624; $\frac{25}{25}$ 1·2588 (Perkin, *C. J.* 45, 507); $\frac{20}{4}$ 1·2590 (Brühl). M.M. 4·111 at 16° (P.). H.F.p. −1364 (Ramsay). μ_β 1·478. R_∞ 33·70 (B.). S.H. ·612 (Winklemann, *P.* 153, 481). *Isotonic coefficient*: 1·78 (De Vries, *Ann. Agr.* 14, 376).

Glycerin, as was first shown by Chevreul, bears the same relation to the fats and fatty oils that alcohol does to acetic ether, and is, therefore, formed from them by boiling with aqueous alkalis, baryta-water, lime-water, litharge and water, or even by heating (under pressure) with water alone. It was discovered in 1779 by Scheele, who obtained it in the preparation of lead plaster by saponifying lard with lead oxide.

Formation.—1. Always produced in the alcoholic fermentation of sugar, the amount being about 3 p.c. of the sugar used (Pasteur, *C. R.* 46, 857; 47, 224). Hence it occurs in all fermented liquors. Wine may contain about 1 p.c. of glycerin. Brandy also may contain a little glycerin (Morin, *C. R.* 105, 1019).—2. When s-tri-bromopropane $CH_2Br.CHBr.CH_2Br$ is heated with AgOAc there is formed glyceryl tri-acetate or triacetin $CH_2(OAc).CH(OAc).CH_2(OAc)$. Baryta-water converts this tri-acetin into glycerin (Wurtz, *A. Ch.* [3] 51, 97).—3. Synthetically prepared from acetone by successive conversion into isopropyl alcohol, propylene, propylene chloro-iodide, propylene chloride, and tri-chloro-propane. The tri-chloro-propane was obtained by heating propylene chloride with iodine chloride at 140°, and was converted into glycerin by heating with water at 180° (Friedel a. Silva, *C. R.* 76, 1594).

Preparation.—1. *By saponification with oxide of lead.*—Five pts. of finely pounded litharge are heated with nine pts. of olive oil or any other glyceride and a small quantity of water, the mixture being stirred, and the water renewed till the oxide of lead is converted into a plaster; the watery liquid is then separated from this plaster, and freed from lead by a stream of H_2S, and the filtrate is evaporated to a syrup over the water-bath. For many years all the glycerin of commerce was obtained by this method; but it was very apt to retain small quantities of lead, the presence of which is very objectionable in any therapeutic application of glycerin.—2. From the alkaline mother-liquor of the soap-works glycerin may be obtained by distillation with superheated steam.—3. By saponifying tallow with lime and water, ppg. excess of lime by H_2SO_4, and evaporating.—4. By distilling fats in a current of superheated steam at 300°; the fats are then decomposed, and the glycerin which distils over is finally rectified *in vacuo*.

Properties.—Thick syrup with sweet taste. Neutral to litmus. Miscible with water, alcohol, and chloroform, but insol. ether. It is slightly volatile with steam (Couttolenc, *Bl.* [2] 36, 133). Volatilisation of glycerin does not, however, take place as long as 50 p.c. of water is present, and even when there is only 26 p.c. water, mere traces of glycerin pass over (Hehner, *An.* 12, 65; *cf.* Nessler a. Barth, *Fr.* 21, 44; 23, 329). When distilled under atmospheric pressure it is partially decomposed, but it may be distilled under diminished pressure without decomposition. It boils at 180° under 12·5 mm. pressure (Bolas, *C. J.* 24, 84). Glycerin is hygroscopic and may absorb as much as 58 p.c. of water from the air (E. Williams, *C. C.* 1881, 76). The following table gives the specific gravity at 20° of solutions of glycerin, compared with water at 20° (Nicol, *Ph.* [3] 18, 302):—

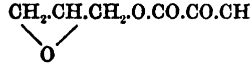
Glycerin per cent.	Specific gravity
100	1·26348
90	1·23720
80	1·21010
70	1·18293
60	1·15561
50	1·12831
40	1·10118
30	1·07469
20	1·04884
10	1·02391

A 10 p.c. solution of glycerin freezes at −1°; a 20 p.c. solution at −2·5°; a 30 p.c. solution at −6°; a 40 p.c. solution at −17·5°; and a 50 p.c. solution at −31°. Pure glycerin may be obtained in deliquescent trimetric crystals melting at 20°: $a:b:c = {·}70:1:{·}66$ (Nitsche, *D. P. J.* 209, 145; Von Lang, *P.* 152, 637). Glycerin burns with a colourless flame. Glycerin dissolves iodine. An aqueous solution of glycerin dissolves more As_2O_3 than pure water (Schiff, *A.* 118, 86). Aqueous solutions of glycerin dissolve baryta, strontia, and lime. Pure glycerin dissolves KOH and NaOH. Glycerin dissolves all deliquescent salts, and also the sulphates of K, Na, and Cu, and the chlorides of K and Na (Pelouze, *A.* 19, 210; 20, 46). Aqueous and even dry glycerin dissolves PbO. $FeCl_3$ mixed with much glycerin is not ppd. by alkalis (*f.* Puls, *J. pr.* 15, 83). Cupric sulphate mixed with glycerin forms, with a small quantity of potash, a pp. which dissolves in excess of potash; but on boiling the resulting deep-blue solution bluish flakes are deposited. Glycerin renders borax solution acid (D. Klein, *C. R.* 86, 826; Senier a. Lowe, *Ph.* [3] 8, 819; *C. J.* 33, 438; Donath a. Mayrhofer, *Fr.* 20, 379; Dunstan, *Ph.* [3] 13, 257).

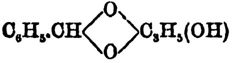
Tests.—Glycerin is optically inactive, so that adulteration with sugar may readily be detected by the polariscope. The presence of glycerin in a saccharine liquid may be detected by mixing with slaked lime and sand, evaporating over a water-bath, and extracting the nearly dry residue with alcohol-ether; the alcohol-ether on evaporation leaves the glycerin behind; a borax bead after dipping in the glycerin colours a flame green (Senier a. Lowe, *C. J.* 33, 438; Donath a. Mayrhofer, *Fr.* 20, 383). If a mixture of equal volumes of glycerin, phenol, and H_2SO_4 be heated to 120°, diluted with water, and treated with NH_3, a crimson colour is developed (Reichl, *B.* 9, 1429).

Estimation.—1. When an aqueous solution is shaken with benzoyl chloride and sufficient NaOH to make it alkaline, an insoluble crystalline pp. is produced, which chiefly consists of the dibenzoyl-derivative $C_3H_5(OBz)_2(OH)$. When crystallised from petroleum-ether it forms long colourless needles [70°], v. sol. alcohol and ether, insol. water. Other hydroxylated compounds must be absent. The reaction can be used for the quantitative determination of glycerin in beverages (E. Baumann, *B.* 19, 3221; Diez, *H.* 11, 472).—2. Commercial glycerin (1 g.) is boiled for 1 hour with (7 g. of) Ac_2O and (3 g. of) dry NaOAc in a flask with inverted condenser; the product is diluted with water (50 c.c.) and heated to boiling. In this operation the glycerin is converted into the tri-acetin, and the amount of tri-acetin can be determined after filtration by neutralisation of free acid by NaOH, saponification with standard NaOH and titration with standard HCl (Benedikt a. Cantor, *M.* 9, 521).—3. Champion and Pellet (*Bl.* [2] 19, 493) estimate the amount of glycerin in commercial samples by treatment with a mixture of nitric acid and H_2SO_4, the resulting nitroglycerin being dried at 100° and weighed.—4. A safer method consists in mixing the liquid (1 pt.) with lead oxide (25 pts.) and evaporating to a constant weight at 130°; the increase in weight of the lead oxide is noted (Morawski, *Fr.* 21, 130).—5. For the estimation of glycerin in *wine*, Macagno (*D. P. J.* 216, 95) digests a litre of the wine with recently precipitated lead hydroxide; evaporates the liquid on the water-bath, then adds a further quantity of lead hydroxide; exhausts the mass with absolute alcohol, and precipitates the dissolved lead by a stream of carbon dioxide. The filtered liquid when evaporated leaves nearly pure glycerin.—6. The estimation of glycerin in wine or beer may be effected by mixing with milk of lime and chalk, evaporating to dryness, and extracting with alcohol. The alcoholic extract is evaporated to a small bulk, mixed with alcohol-ether, filtered if necessary, dried at 105°, and weighed (Weigert, *C. C.* 1888, 1511; *cf.* Claus-nizer, *Fr.* 20, 80). Instead of weighing the glycerin it may be oxidised either by boiling with $K_2Cr_2O_7$ and H_2SO_4, or by heating with $KMnO_4$ and H_2SO_4 at 40°; in either case the amount of carbonic acid evolved or the amount of reduction effected may be noted (Legler, *An.* 12, 14; Hehner, *An.* 12, 44, 65; Planchon, *C. R.* 107, 246; Cross a. Bevan, *C. N.* 55, 2).—7. An aqueous solution of glycerin (about ·25 g.) may be oxidised by $KMnO_4$ after addition of KOH (5 g.), and the oxalic acid formed ppd. as calcium salt (Fox a. Wanklyn, *C. N.* 53, 15; Benedikt a. Zsigmondy, *Fr.* 25, 587; Allen, *An.* 11, 52; Jolles, *Fr.* 27, 521).

Reactions.—1. Partially decomposed by *distillation* yielding acroleïn, acetic acid, CO_2, and polyglyceric compounds. When distilled with P_2O_5 or $KHSO_4$ it yields acroleïn. When distilled with $CaCl_2$ it yields acroleïn, acetone, propionic aldehyde, phenol, &c. (Linnemann a. Zotta, *A. Suppl.* 8, 254; 174, 87).—2. Glycerin is oxidised by the air in presence of *platinum-black* to CO_2 and water; at the same time the so-called glyceric aldehyde (a kind of sugar) is formed. This body is fermentable by yeast (Grimaux, *Bl.* [2] 49, 251; *C. R.* 105, 1175). A substance resembling glucose is also formed by placing glycerin in contact with iron that is undergoing oxidation in moist air (Kosmann, *Bl.* [2] 27, 246).—3. Propionic and formic acids are among the products of the oxidation of glycerin in alkaline solution by ozone (Gorup-Besanez, *A.* 125, 211).—4. MnO_2 and HCl or H_2SO_4 yield CO_2 and formic acid.—5. If fuming nitric acid and dilute glycerin are left in contact in two layers in the cold, gradual oxidation takes place with formation of glyceric, racemic, glycollic, glyoxylic, oxalic, formic, and hydrocyanic acids (Debus, *A.* 106, 79; Beilstein, *A.* 120, 228; Heintz, *A.* 152, 325; Przybytek, *Bl.* [2] 35, 108). By the action of HNO_3 on glycerin in the cold Przybytek (*Bl.* [2] 36, 145; 37, 342) also obtained an acid $C_6H_{10}O_8$, apparently identical with saccharic acid, and inactive tartaric acid, as well as racemic acid. Werigo (*C. C.* 1881, 612) by oxidising glycerin with HNO_3 obtained an acid $C_3H_4O_4$. On warming glycerin with dilute nitric acid (S.G. 1·18) a violent reaction ensues, and after removal of the nitrous acid with urea a liquid is obtained which reduces Fehling's solution and gives with phenyl-hydrazine hydrochloride the crystalline di-phenyl-hydrazide, 'phenyl glycerosazone' $C_{15}H_{16}NO_4$ or $CH_2(OH).C(N_2HPh).CH(N_2HPh)$ [131°] (Fischer a. Tafel, *B.* 20, 1088).—6. If lead hydroxide (500 g.) be added to boiling aqueous (85 p.c.) glycerin (1,000 g.) and, after cooling to 0°, the resulting lead compound be washed with alcohol and ether, dried at 100°, and exposed to bromine vapour, 'glycerose' is formed. It may be extracted by alcohol, and after evaporating the alcohol and treating the residue with $BaCO_3$ to remove acids, it can be dissolved in ether. Glycerose is a syrup which reduces Fehling's solution, ferments with yeast, and when treated with phenyl-hydrazine yields phenyl-glycerosazone. However, it appears to be a mixture, since it yields two oxy- acids when warmed with conc. HCyAq (Fischer a. Tafel, *B.* 21, 2634). If glycerin (10 pts.), $Na_2CO_3 10aq$ (35 pts.), water (60 pts.), and bromine (15 pts.) be mixed at 10° and the solution be mixed with phenyl-hydrazine solution two osazones are got, $C_{18}H_{22}N_4O_4$ [217°] and [159°] (Fischer a. Tafel, *B.* 20, 3384).—7. A mixture of HNO_3 and conc. H_2SO_4 gives the trinitrate, commonly called nitroglycerin.—8. Alkaline $KMnO_4$ forms CO_2, formic acid, propionic, and traces of tartronic acid. The latter is often present as the acid manganese salt $Mn(CO_2.CH(OH).CO_2H)_2$ (Campani a. Bizzarri, *G.* 12, 1). By using strongly alkaline $KMnO_4$, oxalic acid (1 mol.) and CO_2 (1 mol.) were obtained by Fox a. Wanklyn (*C. N.* 53, 15; *cf.* Planchon, *C. R.* 107, 246).—9. A solution of glycerin acidulated with 5 p.c. of H_2SO_4 yields on electrolysis formic paraldehyde (tri-oxy-methylene), formic, acetic, oxalic, and glyceric acids, and a glucose (polymeride of tri-oxy-methylene) which forms a barium compound $C_6H_{12}O_6 3BaO$, is not fermented by yeast, and is oxidised by HNO_3 to oxalic acid (Renard, *A. Ch.* [5] 17, 303). Bartoli a. Papasogli (*G.* 13, 287) obtained acroleïn, formic paraldehyde, glyceric acid, and formic acid by electrolysing glycerin.—10. Lime and Ag_2O form glycollic and formic acids (Kiliani, *B.* 16, 2415).—11. According to Dumas a. Stas (*A.* 35, 158) by gently heating glycerin with KOH it is converted into potassium formate and acetate with evolution of hydrogen. Herter (*B.* 11, 1167) also obtained lactic acid.—12. On distillation with *caustic soda* it is on the one hand reduced to propylene glycol, and on the other hand oxidised to formic acid; other products are methyl, ethyl, and *n*-propyl alcohol, hexylene and other hydrocarbons, acroleïn, and various ketones (Belohoubek, *B.* 12, 1872; Letts, *B.* 5, 159; Fernbach, *Bl.* [2] 34, 146).—13. Distillation of the calcium derivative $CaC_3H_6O_3$ gives methyl, ethyl, and hexenyl alcohols, aldehyde, acetone, di-ethyl-ketone, a ketone $C_6H_{12}O$ (124°), mesityl oxide, and phorone (Destrem, *A. Ch.* [5] 27, 20).—14. By heating with *bromine* and water at 100° glyceric acid and bromoform are produced (Barth, *A.* 124, 341). Bromine dropped into heated dry glycerin forms acroleïn. For the action of bromine and Na_2CO_3 *v. Reaction* 6.—15. HIAq converts glycerin into allyl iodide and propylene; an excess of HI forms isopropyl iodide (Erlenmeyer, *A.* 139, 211). When glycerin is heated with HCl mono- and di-chlorhydrins are formed, together with a crystalline compound [110°], which appears to be a polymeride of epichlorhydrin (Fauconnier a. Sanson, *Bl.* [2] 48, 236). HBr forms mono- and di-bromhydrins.—16. *Iodide of phosphorus* PI_2 forms propylene, allyl iodide, and a little allyl alcohol (Berthelot a. De Luca, *A. Ch.* [3] 43, 257; 44, 350; Henry, *B.* 14, 403). Glycerin may be conveniently converted into allyl iodide by running a solution of iodine (440 g.) in allyl iodide (160 g.) into a heated mixture of glycerin (2,000 g.), iodine (60 g.) and red phosphorus (200 g.) (Béhal, *Bl.* [2] 47, 875). Glycerin (200 g.) may also be converted into allyl iodide by mixing with iodine (135 g.), adding clear phosphorus (40 g.) cautiously and distilling in a current of CO_2. When glycerin (2 pts.) is mixed with iodine (30 pts.) and red phosphorus (5½ pts.) is cautiously added to the cooled mixture, isopropyl iodide is formed, and may be distilled over. Aluminium foil and iodine also form allyl iodide (Hodgkinson, *C. N.* 35, 237).—17. PBr_3 and PBr_5 form mono- and di-bromhydrins and *s*-tri-bromo-propane (Berthelot a. De Luca, *A. Ch.* [3] 48, 304). PCl_3 and PCl_5 act in like manner.—18. S_2Cl_2 forms di-chlorhydrin and *s*-tri-chloro-propane (Carius, *A.* 124, 222; *cf.* Wolff, *A.* 150, 59).—19. When glycerin is distilled with ammonium chloride a chlorinated compound (175°) is formed, together with some acids, and a base 'glycoline' $C_6H_{10}N_2$ (155°). S.G. ^{13} 1·008. This base forms a platinochloride $B''H_2PtCl_6$, a deliquescent crystalline hydrochloride $B''HCl$, and a crystalline ethylo-iodide $B''EtI$ (Étard, *C. R.* 92, 795).—20. When glycerin is heated with acids one or more acid radicles usually displace its hydroxylic hydrogen. Thus acetic acid forms the acetins, citric acid forms the citrins, phosphoric acid forms glycero-phosphoric acid, sulphuric acid gives glycero-sulphuric acid.—21. Excess of *oxalic acid* is split up by glycerin at 100° into formic acid and CO_2 (Berthelot, *A.* 98, 139). When excess of glycerin is heated with oxalic acid at 200°-250° it is reduced to allyl alcohol (Tollens, *A.* 156, 130). Distillation with formic acid also converts glycerin into allyl alcohol (Henninger, *Bl.* [2] 21, 242).—22. When glycerin is distilled with *citric acid* there is formed glycide pyruvate

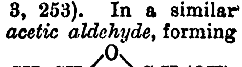


$CH_2.CH.CH_2.O.CO.CO.CH_3$ [82°] (241°) (De Clermont a. Chautard, *C. R.* 105, 520). 23. Distillation with Na_2S gives an oil (58°) whence HgO gives a crystalline compound [35°] (Schlagdenhauffen, *C. R.* 76, 1021).—24. Heated with anhydrous *borax* it forms $NaBO_2$ and the borin $C_3H_5BO_3$ which is decomposed by water into boracic acid and glycerin (Dunstan, *Ph.* [3] 14, 41).—25. Glycerin acts upon benzoic aldehyde at 200°, forming benzylidene-glycerin



$$C_6H_5.CH\langle O_2 \rangle C_3H_5(OH)$$

a liquid that is not volatile under atmospheric pressure, but boils under 20 mm. pressure at 190°-200° (Harnitz-Harnitzky a. Menschutkin, *A.* 136, 127; *Bl.* [2] 3, 253). In a similar manner it reacts with *acetic aldehyde*, forming ethylidene-glycerin



$$CH_3.CH\langle O_2 \rangle C_3H_5(OH)$$

(184°-188°), S.G. $\frac{0}{0}$ 1·081, V.D. 4·162; and with valeric aldehyde forming amylidene-glycerin (224°-228°), S.G. $\frac{0}{0}$ 1·027, V.D. 5·526 (calc. 5·544).—26. Glycerin in dilute solution undergoes fermentation (due to *Bacillus butylicus*?) in presence of chalk forming *n*-butyl alcohol, ethyl alcohol, *n*-propyl alcohol, *n*-amyl alcohol (138°), trimethylene glycol, hexoic, butyric, lactic, and acetic acids, and evolving CO_2 and hydrogen (Fitz, *B.* 9, 1348; 10, 276; 11, 42; 13, 36, 1311; 15, 876; Morin, *C. R.* 105, 816; *cf.* Berthelot, *A. Ch.* [3] 50, 346; Bechamp, *Z.* [2] 5, 663; Hoppe-Seyler, *H.* 3, 353; *C. J.* 40, 82; Freund, *M.* 2, 638).—27. Distillation of glycerin (1 kilo.) with *zinc-dust* (2 kilos.) yields propylene, acroleïn, allyl alcohol, hexenyl alcohol $C_6H_{10}O$ (c. 140°), and a compound $C_{12}H_{20}O_2$ (c. 200°) (Kerstein, *B.* 9, 695; Claus, *B.* 18, 2931).—28. Distillation with *calcium chloride* gives a liquid $C_6H_{10}O_3$ (172°) formerly called glyceryl oxide, but which appears rather to be the anhydride of acetyl-carbinol $(CH_3.CO.CH_2)_2O$. The same liquid is found in the black residue in the preparation of allyl alcohol from glycerin and oxalic acid. It may be reduced by HI to glycerin. It is miscible with water, alcohol, and ether. Water at 100° converts it into glycerin. Br forms dibromhydrin. Sodium-amalgam does not attack it. Chromic acid mixture gives formic acid and acetic aldehyde. Hot dilute HCl converts it into a substance that reduces Fehling's solution and ammoniacal $AgNO_3$ (Linnemann a. Von Zotta, *A. Suppl.* 8, 254; Von Gegerfelt, *B.* 4, 919; Zotta, *A.* 174, 87; Tollens, *Z.* 1871, 528; Tollens a. Loe, *B.* 14, 1947; Silva, *C. R.* 93, 418). 29. *Aniline*, *nitro-benzene*, and H_2SO_4 form quinoline (Skraup, *M.* 2, 139; 3, 381).—30. *Acetamide* and P_2O_5 give (*Py.* 2)-methyl-pyridine (Zanoni, *B.* 15, 528).—31. Heated with *ammonium sulphate* at 255° for seven hours there is formed a mixture of bases of the pyridine series, including pyridine, (*Py.* 2)-methyl-pyridine, and a di-methyl-pyridine (Storch, *B.* 19, 2456, *cf. Reaction* 19).—32. By heating with aniline and $ZnCl_2$ it forms skatole (O. Fischer a. German, *B.* 16, 710).—33. Growing algæ (*Spirogyra*) are capable of converting glycerin into starch (Bokorny, *C. C.* 1888, 858).

Metallic derivatives.—The heat developed by the action of alkalis upon glycerin has been studied by De Forcrand (*C. R.* 103, 596; 104, 116, 291, 361; 106, 665, 746; 107, 269). $NaC_3H_7O_3$. Obtained by heating glycerin with sodium-amalgam or with NaOEt. Prepared by adding glycerin to an alcoholic solution of NaOEt, when radiating stars composed of minute crystals of $NaC_3H_7O_3HOEt$ separate (the ppn. is exothermic, but the ppn. of $C_3H_7NaO_3$ would have been endothermic); when these crystals are heated in a current of dry hydrogen they give off their alcohol of crystallisation (Letts, *C. J.* 25, 450; Blaas, *M.* 2, 785). White deliquescent powder, decomposed by water into NaOH and glycerin. CS_2 heated with it at 55° forms $NaS.CS.O.C_3H_5(OH)_2$; an orange mass, insol. ether, decomposing at 65°, and crystallising from alcohol with HOEt (Löbisch a. Looss, *M.* 2, 372). Glycerin (1 mol.) mixed with a concentrated solution of NaOMe in MeOH deposits $NaC_3H_7O_3HOMe$ in deliquescent needles, which give off MeOH in a stream of hydrogen at 120°. The corresponding $NaC_3H_7O_3HOPr$, $NaC_3H_7O_3HOCH_2Pr$, and $NaC_3H_7O_3HOC_5H_{11}$ may be obtained in like manner (De Forcrand, *C. R.* 104, 291). Sodium-glycerin and methylene chloride form syrupy $(CH_2(OH).CH(OH).CH.O)_2CH_2$ (Höland, *A.* 240, 242). $Na_2C_3H_6O_3$. [220°]. When $NaC_3H_7O_3$ is mixed with alcoholic NaOEt and evaporated at 100° to 120° in hydrogen the residue is $NaC_3H_7O_3NaOEt$, but at 180° the di-sodium derivative $Na_2C_3H_6O_3$ is left (Löbisch a. Looss, *M.* 2, 843; De Forcrand, *C. R.* 106, 665). Deliquescent crystalline mass; readily decomposed by moist air. The compound $Na_3C_3H_5O_3$ has not been obtained.—$KC_3H_7O_3HOEt$: laminæ.—$KC_3H_7O_3$: obtained in the same way as the corresponding Na derivative (De Forcrand, *C. R.* 104, 116). Does not react with KOMe even at 180°. — $KC_3H_7O_3HOMe$. — $KC_3H_7O_3HOPr$. — $KC_3H_7O_3HOC_5H_{11}$. — $BaC_3H_6O_3$. Prepared by heating glycerin with BaO at 50° (Destrem, *C. R.* 90, 1213; *A. Ch.* [5] 27, 17, 44). White deliquescent powder, turning yellow in dry air; decomposed by water into baryta and glycerin. On distillation it gives hydrogen, $BaCO_3$, methane, propylene, and various alcohols of the series $C_nH_{2n}O$.—$CaC_3H_6O_3$. Prepared in the same way as the preceding which it resembles in physical properties. Decomposed on distillation into aldehyde, acetone, di-ethyl-ketone, mesityl oxide, phorone, methyl alcohol, ethyl alcohol, and hexenyl alcohol (D.).—$Pb.C_3H_6O_3$: formed by mixing a hot solution of $Pb(OAc)_2$ (22g.) in water (250 c.c.) with glycerin (20 g.) and KOH (15g.). Slender needles.—$Pb_3(C_3H_5O_3)_2$. A sticky pp. formed by boiling 50 grms. of lead acetate with 250 c.c. water and 25 grms. of PbO, filtering and mixing with 75 grms. of glycerin (S.G. 1·24) and a solution of 20 g. KOH (in 100 c.c. water) which has been boiled with excess of PbO.—$2(C_3H_5O_3Pb.PbNO_3),Pb(OH)NO_3$. Formed by adding NH_3 (2·57 grms.) to a solution of lead nitrate (25 grms.) and glycerin (30 grms.) in water (250 c.c.) (T. Morawski, *J. pr.* [2] 22, 408). $Na_2Mn(C_3H_5O_3)_2$. Formed by boiling hydrated MnO_2 (from $Mn(OAc)_2$ and chlorine) with glycerin and aqueous NaOH (Schottländer, *A.* 155, 230). Yellowish-red mass, insol. alcohol and ether, v. sol. aqueous glycerin. Boiling water decomposes it with ppn. of hydrated MnO_2. Its solution gives pps. with $AgNO_3$, with $Pb(NO_3)_2$ and with $Hg_2(NO_3)_2$.—$SrMn(C_3H_5O_3)_2$. Obtained by dissolving strontium hydroxide (12 pts.) in glycerin (150 pts.) and adding ppd. hydrated manganese dioxide (3 pts.) to the boiling solution. Light ochre-yellow powder.

Glycerin mono-nitrate $C_3H_7NO_5$ *i.e.* $C_3H_5(OH)_2(ONO_2)$. From glycerin and HNO_3 diluted with (3 pts. of) water (Hanriot, *A. Ch.* [5] 17, 118). Liquid, v. e. sol. water, sl. sol. ether. Explodes when struck.

Glyceryl tri-nitrate $C_3H_5(ONO_2)_3$. *Nitro-glycerin.* [−20°]. S.G. 1·60 at 15° S. ·0125; S. (alcohol) 42; S. (MeOH) 125 Mol. w. 227. Prepared by dropping glycerin (dried at 100°) into a mixture of fuming HNO_3 and conc. H_2SO_4 kept below 10°. After some hours the product is poured into water, and the ppd. nitroglycerin dried at 70° (Sobrero, *A.* 64, 398; Williamson, *A.* 92, 305; Boutmy a. Faucher, *Bl.* [2] 27, 383; Matthew Hay, *Tr. E.* 32, 67). Viscid liquid, without odour (when cold) but with sweet taste. Almost insol. water, v. sol. alcohol, ether, chloroform, HOAc, benzene, and phenol; nearly insol. glycerin. Solidifies in a freezing mixture in long needles. Poisonous. When quite pure it may be kept for any length of time, otherwise it gradually decomposes forming glyceric, oxalic, and nitrous acids (De la Rue a. Müller, *A.* 109, 122). When struck it explodes violently. A mixture of nitroglycerin with silica in the form of infusorial earth is called dynamite (Nobel, *D. P. J.* 90, 124). *Reactions.*—1. Alcoholic *potash* forms nitrite, nitrate, acetate, oxalate, and formate of potassium, a reddish-brown resinous mass, and a substance which when dissolved in even 30 volumes of hot alcohol forms a jelly when cold (Hay).—2. *Alkaline carbonates* produce the same quantity of nitrous acid (containing 33 p.c. of the nitrogen) as alcoholic KOH. Ammonia acts in like manner but less energetically. Na_2HPO_4 behaves like NH_3.—3. HClAq decomposes it, as does hot (but not cold) H_2SO_4

4. HIAq decomposes nitro-glycerin into glycerin and NO (Mills, *J.* 1864, 494).—5. Conc. H_2SO_4 and Hg also give off NO by the measurement of which the nitro-glycerin might be estimated (Hempel, *Fr.* 20, 85; Hess, *Fr.* 22, 128).—6. When evaporated with yellow ammonium sulphide it is reduced to glycerin (Bloxam, *C. N.* 47, 169).

Glyceryl tri-nitrite $C_3H_5(NO_2)_3$. (c. 150°). S.G. $\frac{10}{15.5}$ 1·291. *Formation.*—1. Dry nitrous acid gas from As_2O_3 and HNO_3 (S.G. 1·35) passed into cold glycerin forms two layers, the smaller is an aqueous solution of nitrous acid, the larger is impure glyceryl trinitrite $C_3H_5(ONO)_3$. It is purified by distillation in a current of hydrogen (O. Masson, *C. J.* 43, 348). *Properties.*—Boils at about 150° with partial decomposition. Yellowish oil. Burns with whitish flame, does not explode when struck. Bleaches the skin. Sol. ether, chloroform and benzene, but insol. CS_2. With cold glacial acetic acid, it forms a green solution which gives off nitrous fumes when heated. It decomposes spontaneously giving off NO. *Reactions.*—1. H_2SO_4 violently decomposes it.—2. K_2CO_3 forms KNO_2.—3. *Alcohol* forms EtONO.—4. It does not mix with water, but is slowly decomposed by it, glycerin and HNO_2 being apparently formed in the first instance.

Glycero-sulphuric acids:—

Mono-sulphurin $C_3H_5(OH)_2SO_4H$. *Glycerin-sulphuric acid.* From glycerin (1 pt.) and sulphuric acid (2 pts.) (Pelouze, *A. Ch.* 63, 21). Unstable liquid, being decomposed by evaporating its solution even below 0°. It decomposes carbonates forming salts which are v. sol. water and very unstable.—CaA'_2: needles, begins to decompose at 140°, giving off acrolein, acrylic acid, and SO_2 (Redtenbacher, *A.* 47, 118).

Di-sulphurin $C_3H_5(SO_4H)_2(OH)$. Formed by slow action of water on the tri-sulphurin which it much resembles (Claesson, *J. pr.* [2] 20, 6).

Tri-sulphurin $C_3H_5(SO_4H)_3$. *Glyceryl tri-sulphuric acid.* Formed by adding glycerin slowly to chloro-sulphuric acid ($ClSO_3H$) as long as HCl is briskly given off. The crystals obtained are dried over H_2SO_4 (Claesson, *J. pr.* [2] 20, 4). Slowly decomposed by water: $C_3H_5(SO_4H)_3 + H_2O = C_3H_5(SO_4H)_2(OH) + H_2SO_4$. Boiling water decomposes it into glycerin and sulphuric acid.—$Ba_3A'_2$.

Glycero-phosphoric acid $C_3H_9PO_6$ *i.e.* $C_3H_5(OH)_2O.PO(OH)_2$. Exists in small quantity in human urine (Sotnitschewsky, *H.* 4, 214). Obtained from lecithin or the yolk of eggs by boiling with aqueous alkalis or baryta (Gobley, *J. Ph.* [3] 9, 161; Strecker, *C. R.* 52, 1270). Formed by heating glycerin with H_3PO_4 or P_2O_5 (Pelouze, *C. R.* 12, 718). The free acid is decomposed by evaporation of its aqueous solution.

Salts.—BaA″ (Thudichum a. Kingzett, *C. J.* 30, 20).—BaA″aq.—CaA″.—$CaH_2A''_2$.—PbA″: insol. water.

Di-stearyl-glycero-phosphoric acid $C_3H_5(O.C_{18}H_{35}O)_2O.PO_3H_2$. [55°-63°]. Obtained by heating di-stearin with P_2O_5 at 110°. The product is treated with alcohol 85 (p.c.). The residue is extracted with boiling alcohol and filtered; powdered Na_2CO_3 is added to the filtrate when a mixture of sodic phosphate and sodic di-stearyl-glycerophosphate is ppd. This is extracted with hot benzene which dissolves the latter. A mixture of glacial acetic acid and H_2SO_4 liberates the free acid from its sodium-salt (Hundeshagen, *J. pr.* [2] 28, 235). Fat-like mass. Reddens moist litmus. The fused acid swells up when moistened. Sl. sol. hot water and dilute acetic acid, insol. dilute mineral acids, v. sol. aqueous alkalis, glacial acetic acid, alcohol, ether, benzene, and benzoline. Separates from hot solutions in a paste-like mass of small needles. Heated with dilute acids or alkalis it gives glycerin, stearic acid, and phosphoric acid. The ammonium salt is decomposed by heat into NH_3 and the free acid. The sodium salt melts about 180°; on cooling it solidifies to a glassy mass which swells up in warm water forming a mass of globules resembling the myeline condition of lecithin.

Chloride $C_3H_5(O.C_{18}H_{35}O)_2O.PO.Cl_2$. [24°]. From di-stearin (4 pts.) and $POCl_3$ (1 pt.); the product being extracted with ether. The ether is then mixed with alcohol, filtered, and placed over H_2SO_4 and KOH. Wedge-shaped plates. V. sol. alcohol, ether, and benzene. Decomposes at 100°, forming stearic acid. Water soon decomposes it into stearic acid, glycero-phosphoric acid, and HCl.

Neurine salt $C_3H_5(O.C_{18}H_{35}O)_2O.PO(OH).ONMe_3C_2H_4OH$. Prepared by digesting di-stearyl-glycerophosphoric acid with an alcoholic solution of the proper quantity of neurine carbonate. Waxy mass. Sol. alcohol. Swe'ls up in warm water, forming round globules like the myeline form of lecithin. An alcoholic solution of $PtCl_4,2HCl$ gives a pp. of neurine platino-chloride only. Lecithin (*q. v.*), on the other hand, gives a platino-chloride of its own under similar conditions.

Formyl derivative $C_3H_5(OH)_2(OCHO)$. *Monoformin.* Formed by heating glycerin with oxalic acid at 190° (Tollens a. Henninger, *Bl.* [2] 11, 395). Formed also by the action of monochlorhydrin upon sodium formate at 160° (Van Romburgh, *R. T. C.* 1, 186). Decomposed on distillation into CO_2, water, and allyl alcohol.

Di-formyl derivative $C_3H_5(OH)(O.CHO)_2$. *Diformin.* (c. 165° at 20 mm.). S.G. ^{12} 1·304. may be extracted by ether from the residue obtained in preparing formic acid by distilling anhydrous oxalic acid with glycerin (Van Romburgh, *C. R.* 93, 847). Liquid, sol. alcohol, ether, and chloroform, insol. CS_2. Inactive to light. Decomposed by water into formic acid and glycerin. Decomposed by distillation into water, CO_2, and allyl formate. When heated with anhydrous oxalic acid it gives off CO_2 and formic acid, and may therefore be an intermediate product in the preparation of formic acid. When heated with glycerin (5 pts.) at 220° it gives CO, CO_2, and allyl alcohol.

Mono-acetyl derivative $C_5H_{10}O_4$ *i.e.* $C_3H_5(OH)_2(OAc)$. Mol. w. 134. S.G. 1·20. Obtained by heating a mixture of equal volumes of glycerin and glacial acetic acid at 100° for a long time (Berthelot, *A. Ch.* [3] 41, 277; Berthelot a. De Luca, *A. Ch.* [3] 52, 433). Neutral liquid, having a faint ethereal odour. Miscible with ether. When mixed with half its bulk of water it forms a clear liquid, which becomes turbid on addition of a larger quantity of water, by which it is partially decomposed. With alcohol and HCl it yields glycerin and acetic ether.

Di-acetyl derivative $C_7H_{12}O_5$ *i.e.* $C_3H_5(OH)(OAc)_2$. *Diacetin.* Mol. w. 176. (280°). S.G. $\frac{16\cdot5}{}$ 1·184. Formed by heating glycerin (1 pt.) with glacial acetic acid (4 or 5 pts.) at 200°. Liquid; becomes viscid at −40°. Scarcely attacked by AcCl (Hubner a. Müller, *Z.* 1870, 344).

Di-acetyl derivative $C_3H_5(OH)(OAc)_2$. (252°). S.G. $\frac{23}{}$ 1·148. From epichlorhydrin and AgOAc (Laufer, *J.* 1876, 343).

Triacetyl derivative $C_9H_{14}O_6$ *i.e.* $C_3H_5(OAc)_3$.

Triacetin. Glyceryl triacetate. Mol. w. 218. (268° i. V.). S.G. $\frac{8}{}$ 1·174. S. 18, at 27°. Occurs in some fats, as in the oil from the seed of the spindle-tree (*Euonymus europæus*) (Schweizer, *J. pr.* 53, 437). Formed by heating diacetin with glacial acetic acid (18 pts.) for 3 hours at 250°. Formed also by heating *s*-tri-bromo-propane with AgOAc (Wurtz, *A.* 102, 339). Prepared by boiling glycerin (150 pts.) with HOAc (300 pts.) for 40 hours, fractionally distilling the product, dissolving in water, and extracting with ether (H. Schmidt, *A.* 200, 99). The rate of etherification of glycerin by acetic acid has been studied by Menschutkin (*B.* 13, 1814). Liquid, sol. dilute alcohol and ether.

Mono-butyryl derivative $C_7H_{14}O_4$ *i.e.* $C_3H_5(OH)_2(O.CO.Pr)$. S.G. $\frac{17}{}$ 1·088. S. 267. From butyric acid and glycerin by heating for 3 hours at 200° (Berthelot, *A. Ch.* [3] 41, 261). Neutral liquid; mixes with $\frac{3}{8}$ vol. of water, but on adding more water the solution becomes turbid. Decomposed by alkalis and alkaline earths into glycerin and butyric acid. Alcohol and HCl yield butyric ether and glycerin.

Di-butyryl derivative $C_3H_5(OH)(O.CO.Pr)_2$. (320°). S.G. $\frac{17}{}$ 1·083. Formed by heating glycerin with butyric acid for several hours at 275°. Liquid. Not solid at −40°. Aqueous NH_3 decomposes it, forming butyramide.

Tri-butyryl derivative $C_3H_5(O.CO.Pr)_3$. (285°). S.G. $\frac{22}{}$ 1·052. Occurs in butter, along with other glycerides. Obtained by heating mono-butyrin (1 pt.) with butyric acid (15 pts.) at 240° for 4 hours (Berthelot). Formed also by boiling glycerin (1 mol.) with butyric acid (3 mols.) for 60 hours (Lebedeff, *H.* 6, 150). Oil, v. sol. alcohol and ether.

Mono-valeryl derivative $C_3H_5(OH)_2(O.CO.C_4H_9)$. S.G. $\frac{16}{}$ 1·100. Formed by heating valeric acid with excess of glycerin for 3 hours at 200°. Mixes with half its bulk of water, but the solution becomes turbid on further addition of water. Alcohol and HCl form valeric ether and glycerin. NH_3Aq gives valeramide.

Di-valeryl derivative $C_3H_5(OH)(O.CO.C_4H_9)_2$. S.G. $\frac{18}{}$ 1·059. From glycerin and valeric acid at 275°. Oil, with fishy odour. Becomes semi-solid at −40°.

Tri-valeryl derivative $C_3H_5(O.CO.C_4H_9)_3$. From glycerin (1 pt.) and valeric acid (9 pts.) at 220°. Oil; sol. alcohol and ether. Occurs in the oil of *Delphinus globiceps* (Chevreul).

Mono-benzoyl derivative $C_3H_5(OH)_2(OBz)$. *Benzoïcin.* S.G. $\frac{16\cdot5}{}$ 1·228. Formed by heating benzoic acid with excess of glycerin at 200° (Berthelot, *A. Ch.* [3] 41, 290). Thick viscid oil, insol. water, sl. sol. CS_2, v. sol. alcohol and ether. Decomposes at 320°, giving off acroleïn and benzoic acid.

Di-benzoyl derivative $C_3H_5(OH)(OBz)_2$. [70°]. From glycerin, BzCl, and dilute NaOH (E. Baumann, *B.* 19, 3221). Long needles (from ligroïn); insol. water, v. e. sol. alcohol and ether.

Tri-benzoyl derivative $C_3H_5(OBz)_3$. *Tribenzoïcin.* [74°]. S.G. $\frac{12}{}$ 1·228. Obtained by heating benzoïcin with benzoic acid (12 pts.) for 4 hours at 250° (B.). Formed also by heating epichlorhydrin with HOBz; or from epibromhydrin and KOBz at 200° (Van Romburgh, *R. T. C.* 1, 46, 143). Large needles (from ether). V. e. sol. ether, v. sol. boiling alcohol, sl. sol. ligroïn.

o-Oxy-benzoyl derivative $C_3H_5(OH)_2(O.CO.C_6H_4.OH)$. S.G. 1·1366. From salicylic acid, glycerin, and HCl at 100° (Göttig, *B.* 10, 1817). Colourless liquid; v. sol. alcohol, ether, and CS_2.

Benzoyl-succinyl derivative $C_{14}H_{14}O_6$ *i.e.* $C_2H_4(C_2O_2)O_2.C_3H_5.OBz$. *Benzosuccinin.* Formed by heating glycerin with benzoic and succinic acids at 200° (Van Bemmelen, *J. pr.* 69, 84). Soft mass, decomposed by boiling water or alcohol, more readily by alkalis, into glycerin, benzoic acid, and succinic acid.

Tri-myristyl derivative $C_{45}H_{86}O_6$ *i.e.* $C_3H_5(O.C_{14}H_{27}O)_3$. [55°] (Masino, *A.* 202, 173); [46°] (in Otoba). Occurs in nutmegs (from *Myristica moschata*), from which it may be extracted by ether (Playfair, *A.* 37, 155; Comar, *J.* 1859, 366; *Cimento*, 9, 185). Occurs also in otoba, a fatty substance derived from *Myristica Otoba* (Uricœchea, *A.* 91, 369). Crystallises from ether in laminæ. Split up by boiling alkalis into glycerin and myristic acid.

Mono-palmityl derivative $C_{19}H_{38}O_4$ *i.e.* $C_3H_5(OH)_2(O.C_{16}H_{31}O)$. *Monopalmitin.* [58°] (B.); [63°] (C. a. S.). S. (alcohol) 5·306 at 22·5°. Obtained by heating a mixture of glycerin and palmitic acid for 24 hours at 200°; the product is shaken with lime-water and extracted with ether, from which tripalmitin separates first, then dipalmitin, and finally monopalmitin (Berthelot; Chittenden a. Smith, *Am.* 6, 225). Radiating prisms; may be distilled *in vacuo*, but is decomposed when heated under atmospheric pressure, yielding acroleïn and other products.

Di-palmityl derivative $C_{35}H_{68}O_5$ *i.e.* $C_3H_5(OH)(O.C_{16}H_{31}O)_2$. *Dipalmitin.* [50°] (B.); [61°] (C. a. S.). S. (alcohol) ·210 at 20°. Formed by heating palmitic acid with glycerin for 14 hours at 100° (B.). Tables or needles. Like the other palmitins, it is rapidly saponified by water and PbO at 100°.

Tri-palmityl derivative $C_{51}H_{98}O_6$ *i.e.* $C_3H_5(OC_{16}H_{31}O)_3$. *Tripalmitin.* Mol. w. 806. [62°]. S. (alcohol) ·0043 at 21°. Occurs in those natural fats that yield palmitic acid on saponification (*v.* FATS and ACIDS). Obtained from palm oil by expressing the liquid portion, washing the residue with boiling alcohol, and crystallising it from ether (Stenhouse, *A.* 36, 54). It may be formed by heating monopalmitin (1 pt.) with palmitic acid (10 pts.) for 28 hours at 250° (Berthelot). Crystalline mass, v. sl. sol. alcohol, v. e. sol. ether. According to Duffy (*C. J.* 5, 197) some varieties of natural palmitin melt at 46°.

Mono-stearyl derivative $C_{21}H_{42}O_4$ *i.e.* $C_3H_5(OH)_2(O.C_{18}H_{35}O)$. *Monostearin.* [62°]. Prepared by heating stearic acid with excess of glycerin at 220° as long as the former increases in volume. The upper layer is recrystallised from alcohol and ether (Berthelot, *A. Ch.* [3] 41, 221; F. Hundeshagen, *J. pr.* [2] 28, 226). Dendritic groups of needles. Readily soluble in warm alcohol and ether. May be distilled *in vacuo*. Easily saponified by alcoholic potash. Gives off acroleïn when strongly heated.

Di-stearyl derivative $C_{39}H_{76}O_5$ *i.e.* $C_3H_5(OH)(OC_{18}H_{35}O)_2$. *Di-stearin.* [77°]. S. (alcohol) ·7 at 78°. Prepared by heating monostearin with the calculated quantity of stearic acid at 180° as long as water is evolved. Crystallised from alcohol and then from benzoline (Berthelot; Hundeshagen). Clumps of glittering plates (from alcohol); or small spheroids, formed of radiating clusters of minute needles (from ether, ligroin, benzene, and $CHCl_3$). Saponified by alcoholic KOH. Metallic derivatives. — $C_3H_5O_3(C_{18}H_{35}O)_2ONH_4$. From NH_3 and an ethereal solution of di-stearin.— $C_3H_5O_3(C_{18}H_{35}O)_2ONa$. Acetyl derivative.— $C_3H_5O_3(C_{18}H_{35}O)_2Ac$. [30°].

Tri-stearyl derivative $C_{57}H_{110}O_6$ *i.e.* $C_3H_5(O.C_{18}H_{35}O)_3$. *Tristearin. Stearin.* [55°] and [72°]. S.G. (liquid) ·925 at 66°. Occurs in many fats, especially in the solid tallows and lards from animals (Chevreul, *Recherches sur les corps gras*; Braconnot, *A. Ch.* 93, 225; Vogel, *A. Ch.* 58, 154; Lecanu, *A.* 12, 25; Liebig a. Pelouze, *A.* 19, 264; Redtenbacher, *A.* 35, 195; Francis, *A.* 42, 254; Arzbächer, *A.* 70, 239; Heintz, *P.* 84, 221; Duffy, *C. J.* 5, 197, 303; Berthelot, *Chimie Organique*, 2, 52; *A. Ch.* [3] 41, 216, 432; 47, 297; Kopp, *A.* 93, 194; Bouis, *C. R.* 45, 35; Bouis a. Pimentel, *C. R.* 44, 1355). It is very difficult to free stearin from palmitin by fractional crystallisation, but it may be obtained from the fat of the seeds of *Brindonia indica*. Best prepared in a pure state by heating monostearin (1 pt.) with stearic acid (18 pts.) at 270° for 3 hours (Berthelot); or by heating glycerin with stearic acid for 24 hours at 200° (Heintz, *A.* 92, 300). Pearly nodules or laminæ and slender needles. V. sl. sol. cold alcohol, v. sol. boiling alcohol, v. e. sol. ether. Has no taste or odour. May be distilled *in vacuo*. When heated it melts at 55°, but when further heated it becomes solid again, and finally melts at 72°. These two melting-points are lowered by impurities, thus when the stearin has been prepared from fats they may be 52° and 62° respectively. According to Duffy this phenomenon may be explained by assuming the existence of three modifications of stearin.

Arachyl derivative $C_{23}H_{46}O_4$ *i.e.* $C_3H_5(OH)_2(OC_{20}H_{39}O)$. From arachic acid and glycerin (Berthelot, *A. Ch.* [3] 47, 355). Granules, v. sl. sol. cold ether.

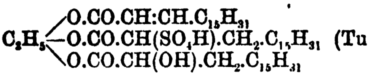
Di-arachyl derivative $C_{43}H_{84}O_5$ *i.e.* $C_3H_5(OH)(OC_{20}H_{39}O)_2$. [75°]. Slender grains. V. sl. sol. cold ether.

Tri-arachyl derivative $C_{63}H_{122}O_6$ *i.e.* $C_3H_5(O.C_{20}H_{39}O)_3$. *Triarachin.* Occurs in the kernels of *Nephelium lappaceum*, and probably also in butter and in the oil from the ground nut (*Arachis hypogæa*) (Goldschmiedt, *J.* 1877, 728; *Sitz. W.* [2] 74, 394; Oudemans, *Z.* 1867, 256; Gössmann, *A.* 89, 1). Sl. sol. ether.

Mono-oleyl derivative $C_{21}H_{40}O_4$ *i.e.* $C_3H_5(OH)_2(OC_{18}H_{33}O)$. *Mono-oleïn.* S.G. ^{21} ·947. Formed by heating oleïc acid with excess of glycerin for 18 hours at 200° (Berthelot). Oil; may be solidified.

Di-oleyl derivative $C_{39}H_{72}O_5$ *i.e.* $C_3H_5(OH)(OC_{18}H_{33}O)_2$. S.G. ^{21} ·921. Oil.

Tri-oleyl derivative $C_{57}H_{104}O_6$ *i.e.* $C_3H_5(OC_{18}H_{33}O)_3$. *Tri-oleïn. Oleïn.* The chief constituent of fatty oils; occurs also in solid fats. May be formed by heating glycerin with excess of oleïc acid at 240° (Berthelot). Oil. May be distilled *in vacuo*. Decomposed by distillation under atmospheric pressure, *n*-hexane and *n*-heptane being among the products (Engler, *B.* 22, 594). Slowly saponified by water and PbO at 100°. V. sl. sol. alcohol, v. e. sol. ether. Conc. H_2SO_4 converts it into oily



$$C_3H_5\left\langle\begin{array}{l}O.CO.CH{:}CH.C_{15}H_{31}\\ O.CO.CH(SO_4H).CH_2.C_{15}H_{31}\\ O.CO.CH(OH).CH_2.C_{15}H_{31}\end{array}\right.$$

(Turkey red oil) (Geitel, *J. pr.* [2] 37, 85). Nitrous acid converts it into the isomeric solid elaidin, a crystalline substance, almost insol. alcohol, v. e. sol. ether, melting at [38°] (Duffy, *C. J.* 5, 197).

Glycero-tartaric acid $C_7H_{12}O_8$ *i.e.* $C_3H_5(OH)_2.O.CO.CH(OH).CH(OH).CO_2H$. Formed by heating equivalent quantities of glycerin and tartaric acid to about 150° (Berzelius, *Handbuch*; Des Plats, *C. R.* 49, 216). Semi-solid mass; insol. ether, v. sol. alcohol, slowly resolved by water into glycerin and tartaric acid. –CaA'_2 3aq: deliquescent amorphous mass.—BaA'_2.

Glycero-di-tartaric acid $C_{11}H_{16}O_{13}$ *i.e.* $C_3H_5(OH).(O.CO.CH(OH)CH(OH).CO_2H)_2$. From glycerin (1 pt.) and tartaric acid (1 pt.) by heating at 100° for 50 hours. An acid $C_{11}H_{14}O_{12}$ is formed at the same time.

Glycero-tri-tartaric acid $C_{15}H_{22}O_{19}$. Formed by heating glycerin (1 pt.) with tartaric acid (20 pts.) at 140°. Tetrabasic acid.

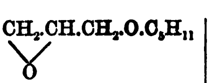
Mono-ethyl ether $C_5H_{12}O_3$ *i.e.* $C_3H_5(OH)_2(OEt)$ or $CH_2(OH).CH(OH).CH_2OEt$. (225°–230°). Formed by heating chlorhydrin with NaOEt at 200°, treating the residue with water, then with K_2CO_3, agitating with ether, and fractionally distilling the extract (Reboul, *A. Ch.* [3] 9, 5). Liquid, sol. water, but separated therefrom by K_2CO_3.

Di-ethyl ether $C_7H_{16}O_3$ *i.e.* $CH_2(OEt).CH(OH).CH_2(OEt)$. (191°). S.G. ·92. Formed by the action of NaOEt on dichlorhydrin (Reboul); or by heating glycerin with KOH and EtBr (Berthelot).

Tri-ethyl derivative $C_9H_{20}O_3$ *i.e.* $C_3H_5(OEt)_3$. *Triethylin.* (180°–190°). From the preceding by successive treatment with PCl_5 and NaOEt (Reboul a. Lourenço, *C. R.* 52, 466). Oil.

Isoamyl derivative $C_8H_{18}O_3$ *i.e.* $C_3H_5(OH)_2(OC_5H_{11})$. *Isoamylin.* (261°). S.G.

$^{\underline{20}}$ ·98. Formed by heating



$CH_2.CH.CH_2.O.C_5H_{11}$ (O bridging the first two C)

with water for some hours at 200° (Reboul). Oil.

Di-isoamyl derivative $C_{13}H_{28}O_3$ *i.e.* $C_3H_5(OH)(OC_5H_{11})_2$. (273°). S.G. $^{\underline{2}}$ ·907. From dichlorhydrin and $NaOC_5H_{11}$.

Ethyl-isoamyl derivative $C_{10}H_{22}O_3$ *i.e.* $C_3H_5(OH)(OEt)(OC_5H_{11})$. (239°). S.G. ·92. From the mono-isoamylin by successive treatment with fuming HCl and NaOEt. Oil.

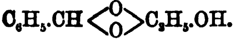
Mono-allyl derivative $C_6H_{12}O_3$ *i.e.* $C_3H_5(OH)_2(OC_3H_5)$. (240°). S.G. $^{\underline{0}}$ 1·116. Occurs in the syrupy liquid left in the preparation of allyl alcohol by heating oxalic acid with excess of glycerin (Tollens, *B.* 5, 68; *A.* 156, 149). Liquid, m. sol. water. Br forms oily $C_6H_{12}Br_2O_3$.

Tri-allyl derivative $C_{12}H_{20}O_3$ *i.e.* $C_3H_5(OC_3H_5)_3$. *Tri-allylin.* (232°). From glycerin, allyl iodide, and KOH (Berthelot a. De Luca, *A.* 100, 361).

Di-phenyl derivative $C_{15}H_{16}O_3$ *i.e.* $CH_2(OPh).CH(OH).CH_2(OPh)$. [81°]. Formed by adding *s*-dichlorhydrin (70 g.) to phenol (100 g.) and KOH (60 g.) (Rössing, *B.* 19, 64). Pearly plates (from alcohol). Insol. water, m. sol. alcohol, v. e. sol. ether. When heated with AcCl (1 mol.) it gives $C_{15}H_{15}AcO_3$ [71°], but with 4 pts. AcCl it forms liquid $C_{21}H_{22}O_6$. In like manner BzCl (1 mol.) forms $C_{15}H_{15}BzO_3$ [67°] but boiling BzCl (7 pts.) forms oily $C_{36}H_{28}O_6$. Forms a stable sodium derivative $C_{15}H_{15}NaO_3$. On sulphonation it gives the disulphonic acid $CH(OH)(CH_2O.C_6H_4.SO_3H)_2$, of which the salt K_2A'' 2aq is v. sol. water.

Di-nitro-phenyl derivative $C_9H_{10}N_2O_7$ *i.e.* $C_3H_5(OH)_2.OC_6H_3(NO_2)_2$. [c. 83°]. From chloro-*m*-di-nitro-benzene, glycerin, and KOHAq (Willgerodt, *B.* 12, 764).

Benzylidine derivative



$C_6H_5.CH\langle{}^{O}_{O}\rangle C_3H_5.OH$. From glycerin and benzoic aldehyde at 200° (Harnitzky a. Menschutkin, *A.* 136, 127). Oil. Decomposed by water.

***u*-Chlorhydrin** $C_3H_7ClO_2$ *i.e.* $CH_2Cl.CH(OH).CH_2OH$.

Chloro-propylene glycol. Mol. w. 110½. (213°) (Hanriot). S.G. $^{\underline{0}}$ 1·338. Formed, together with smaller quantities of the isomeric $CH_2(OH).CHCl.CH_2OH$, by saturating glycerin with HCl and keeping the liquid for some hours at 100° (Berthelot, *A. Ch.* [3] 41, 296). Formed also by heating epichlorhydrin with water (Reboul; Hanriot, *A. Ch.* [5] 17, 62).

Preparation.—The product of the action of dry HCl on damp glycerin in sealed tubes at 100° is distilled under 18 mm. pressure, the *u*-chlorhydrin passing over at 139°, the *s*-isomeride at 146° (Hanriot). There is obtained about 16 times as much of the *u*- as of the *s*-chlorhydrin.

Properties.— Liquid, miscible with water, alcohol, and ether. Unless quite free from HCl it suffers condensation when distilled.

Reactions.—1. *Sodium amalgam* reduces it to propylene-glycol (Lourenço, *C. R.* 52, 1043; Buff, *Bl.* [2] 10, 123).—2. *Potassium cyanide* forms a nitrile which is decomposed on distillation, but is converted by boiling with dilute HNO_3 into di-oxy-butyric acid (Hanriot, *C. R.* 86, 1139; *Bl.* [2] 27, 256).—3. *Baryta* acting on its ethereal solution forms small quantities of glycide and epichlorhydrin.—4. When heated with an aqueous solution of *trimethylamine* in sealed tubes it yields $C_3H_5(OH)_2NMe_3Cl$ and $C_3H_5(OH)_2NMeH_2Cl$. The former gives a crystalline platinochloride $(C_3H_5(OH)_2NMe_3Cl)_2PtCl_4$ and aurochloride $C_3H_5(OH)_2NMe_3AuCl_4$ (Hanriot; V. Meyer, *Z.* [2] 5, 439).

Di-nitrate $CH_2Cl.CH(O.NO_2).CH_2(O.NO_2)$. S.G. $^{\underline{0}}$ 1·511. From chlorhydrin, H_2SO_4, and HNO_3 (Henry, *A.* 155, 164).

Di-formyl derivative $CH_2Cl.CH(OCHO).CH_2(OCHO)$. (185°-195°) at 22 mm. Formed from the chlorhydrin by heating with nitro-methane at 180° (Pfungst, *J. pr.* [2] 34, 36).

Acetyl derivative $C_2H_3(OH)(OAc).CH_2Cl$. (250°). *Aceto-chlorhydrin.* Formed, together with dichlorhydrin, by passing HCl into a mixture of acetic acid and glycerin at 100°; also, together with the following, by the action of AcCl on glycerin (Berthelot a. De Luca, *A. Ch.* [3] 52, 433). From epichlorhydrin and HOAc at 100° (Reboul, *A. Suppl.* 1, 232).

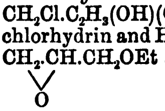
Di-acetyl derivative $CH_2(OAc).CH(OAc).CH_2Cl$. (245°). S.G. ^{4} 1·243. From acetyl chloride and a mixture of equal volumes of glycerin and HOAc (Berthelot a. De Luca, *A. Ch.* [3] 52, 401; *cf.* Franchimont, *R. T. C.* 1, 43). Also from epichlorhydrin and Ac_2O at 180°, a compound $C_{11}H_{17}ClO_7$ (240° at 20 mm.) being formed at the same time (Truchot, *A.* 138, 299).

Di-palmityl derivative $C_3H_5Cl(OC_{16}H_{31}O)_2$. [44°]. From glycerin and palmityl chloride (Villier, *B.* 9, 1933).

Stearyl derivative $C_3H_5Cl(OH)(OC_{18}H_{35}O)$. [28°]. Produced by passing HCl into a mixture of stearic acid and glycerin (Berthelot).

Benzoyl derivative $C_3H_5Cl(OH)(OBz)$. [−40°]. From glycerin, HOBz, and HCl (Berthelot, *A. Ch.* [3] 41, 302).

Ethyl derivative $CH_2Cl.C_2H_3(OH)(OEt)$? (188°). From epichlorhydrin and HOEt at 180°. Formed also from



$CH_2.CH.CH_2OEt$ (O bridging the first two C)

and HCl (Reboul, *A. Suppl.* 1, 236).

Isoamyl derivative $CH_2Cl.C_2H_3(OH)(OC_5H_{11})$. (235°). S.G. $^{\underline{20}}$ 1·0. Formed from epichlorhydrin and isoamyl alcohol at 220° (Reboul).

***s*-Chlorhydrin** $CH_2(OH).CHCl.CH_2(OH)$. *Chloro-trimethylene glycol.* (145° at 10 mm.). S.G. $^{\underline{0}}$ 1·328. Occurs in small quantity among the products of the action of HCl on glycerin at 100°, and may be isolated by fractional distillation *in vacuo* (Hanriot, *C. R.* 86, 1139; *A. Ch.* [5] 17, 73). Formed also by the action of HOCl on allyl alcohol (Henry, *A.* 155, 322). Liquid, resembling the *u*-isomeride. It has a great tendency to form polyglyceric derivatives.

Acetyl derivative $CH_2(OH).CHCl.CH_2(OAc)$. (230°). S.G. $^{\underline{2}}$ 1·27. From allyl acetate and HOCl.

Ethyl derivative $CH_2(OH).CHCl.CH_2(OEt)$. (183°). S.G. ^{11}

1·117. From ethyl allyl oxide and HOCl (Lauch, *B.* 18, 2287). Thick liquid.

Di-ethyl derivative $CH_2(OEt).CHCl.CH_2(OEt)$. (184°). S.G. ^{17} 1·005. From di-ethyl-glycerin and PCl_5 (Reboul a. Lourenço, *A.* 119, 237).

Dichlorhydrins *v.* DI-CHLORO-PROPYL ALCOHOLS.

Chloro-bromhydrins $CH_2Br.C_2H_3Cl(OH)$. (198°). S.G. ^{12} 1·740. From allyl bromide and HOCl (obtained from chloride of lime and boric acid) (Lauch, *B.* 18, 2288). Also from epichlorhydrin and HBr and from epibromhydrin and HCl (Reboul, *A. Suppl.* 1, 225). Liquid. Conc. KOHAq gives epichlorhydrin.

Acetyl derivative $C_3H_5BrCl(OAc)$. (228°). From glycerin, AcCl, and AcBr (Berthelot a. De Luca, *A. Ch.* [3] 52, 462). Sl. sol. water.

Ethyl derivative $C_3H_5BrCl(OEt)$. (187°). From epichlorhydrin and EtBr (Reboul a. Lourenço, *A.* 119, 238).

Bromhydrin $C_3H_7BrO_2$ *i.e.* $CH_2(OH).CHBr.CH_2(OH)$? (180° at 10mm.). Formed by adding glycerin (500 g.) in small portions to liquid bromide of phosphorus (550 g.), the liquid being kept cool and the product after 24 hours fractionally distilled *in vacuo* (Berthelot a. De Luca, *A. Ch.* [3] 48, 304; 52, 433). Oil, sol. ether. In its preparation there is also formed C_6H_9BrO (below 200°) and crystalline $C_6H_9Br_2P$ which is not affected by aqueous KOH at 100°.

Acetyl derivative $C_3H_5Br(OH)(OAc)$. (170°-180°) at 10 mm. Prepared by the action of AcBr (1·5 pts.) on dry glycerin (1·2 pts.) the crude product being distilled under 10 mm. pressure; the yield is good (2·2 pts.) (Hanriot, *A. Ch.* [5] 17, 84). Reduced by the copper-zinc couple to tri-methylene glycol.

Di-ethyl derivative $C_3H_5Br(OEt)_2$. (195°-205°). S.G. ^{8} 1·258. From di-ethyl-glycerin and PBr_5 (Henry, *B.* 4, 704).

Bromhydrin $C_3H_7BrO_2$ *i.e.* $CH_2(OH).CH(OH).CH_2Br$. (138° at 17 mm.). A product of the action of Br on allyl alcohol in presence of water (Fink, *M.* 8, 561). By the action of HBr on dry glycerin, Veley (*C. N.* 47, 39) obtained a bromhydrin (160°) at 60 mm.; S.G. $_{7}$ 1·717.

Di-bromhydrins *v.* DI-BROMO-PROPYL ALCOHOLS.

Tri-bromhydrin *v.* TRI-BROMO-PROPANE.

Iodhydrin $C_3H_5(OH)_2I$. S.G. ^{13} 2·03. From chlorhydrin and KI (Reboul, *A. Ch.* [3] 60, 5).

Di-iodhydrin *v.* DI-IODO-PROPYL ALCOHOL.

Chloro-iodhydrin *v.* CHLORO-IODO-PROPYL ALCOHOL.

Methyl derivative $C_3H_5ClI(OMe)$. (c. 200°). Formed by heating epichlorhydrin (1 mol.) with MeI (1 mol.) at 190°; the yield being 20 p.c. of the theoretical (Paal, *B.* 21, 2971). Oil, volatile with steam.

Ethyl derivative $C_3H_5ClI(OEt)$. (200°-210°).

Isopropyl derivative $C_3H_5ClI(OPr)$. (208°-212°).

n-Propyl derivative $C_3H_5ClI(OPr)$. (200°-210°).

Diglycerin $C_6H_{14}O_5$ *i.e.* $C_3H_5(OH)_2.O.C_3H_5(OH)_2$. *Pyroglycerin.* (220°-230°) at 10 mm. When glycerin, diluted with one-third of its bulk of water, is saturated at 100° with HCl, then mixed with an equal bulk of glycerin, and heated with inverted condenser for 13 hours at 120°, there is obtained a mixture of dichlorhydrin, diglycerin chlorhydrin, diglycerin dichlorhydrin, diglycerin, and triglycerin; these may be separated by fractional distillation *in vacuo* (Lourenço, *C. R.* 52, 359). Thick liquid, insol. ether, sl. sol. cold, v. sol. hot water, miscible with alcohol.

Mono-stearyl derivative $C_3H_5(O.C_{18}H_{35}O)(OH).O.C_3H_5(OH)_2$. [about 30°]. Formed by heating glycerin alone for some time and then with stearic acid for several days at 240°. Crystallised from alcohol (Hundeshagen, *J. pr.* [2] 28, 252). Wax-like solid, sol. ether. Readily saponified by alcoholic potash.

Tri-ethyl derivative $C_{12}H_{26}O_5$ *i.e.* $C_3H_5(OH)(OEt).O.C_3H_5(OEt)_2$. (c. 290°). S.G. ^{14} 1·90. Formed, together with di-ethyl-glycerin and tetra-ethyl-triglycerin, by the action of NaOEt on epichlorhydrin (Reboul a. Lourenço, *C. R.* 52, 401). Liquid, sol. water, alcohol, and ether. Ppd. from its aqueous solution by K_2CO_3.

Diglycerin chlorhydrin $C_6H_{13}ClO_4$. (270°). Formed together with diglycerin dichlorhydrin $C_6H_{12}Cl_2O_4$ by heating glycerin saturated with HCl. By heating either chlorhydrin with alcoholic KOH at 100° there is formed pyroglycide $C_6H_{12}O_4$ (245°-255°). This body is also got by heating polymerised glycide acetate with NaOH (Breslauer, *J. pr.* [2] 20, 193). It is miscible with water and alcohol.

Di-ethyl derivative of diglycerin chlorhydrin $C_{10}H_{21}ClO_4$ *i.e.* $OC_6H_{10}(OH)(OEt)_2Cl$. (285°). S.G. ^{17} 1·11. Formed by heating di-ethyl-glycerin with epichlorhydrin at 200°. Formed also, together with ethyl- and di-ethyl-chlorhydrin, by heating epichlorhydrin with alcohol at 200°. Liquid, sl. sol. water, miscible with alcohol and ether.

Acetyl derivative of diglycerin trichlorhydrin $C_8H_{13}Cl_3O_3$ *i.e.* $OC_6H_{10}(OAc)Cl_3$. (190°) at 20 mm. A product of the action of AcCl on epichlorhydrin (Truchot, *A.* 140, 245).

Triglycerin $C_9H_{20}O_7$ *i.e.* $C_3H_5(OH)_2.O.C_3H_5(OH).O.C_3H_5(OH)_2$. (275°-285°) at 10 mm. Formed as described under diglycerin. Thick liquid.

Tetra-ethyl derivative of triglycerin $C_{17}H_{36}O_7$ *i.e.* $C_9H_{15}O_2(OH)(OEt)_4$. (200°) at 10 mm. S.G. ^{14} 1·022. A product of the action of NaOEt on epichlorhydrin. Liquid, sol. water, alcohol and ether.

Acetyl derivative of triglycerin tetra-chlorhydrin $C_{11}H_{18}Cl_4O_4$ *i.e.* $C_9H_{15}O_2(OAc)Cl_4$. (260°) at 20 mm. From epichlorhydrin and AcCl at 100° (Truchot, *A.* 140, 245).

Hexaglycerin bromhydrin $C_{18}H_{27}BrO_7$. One of the products of the action of PBr_3 on glycerin. Crystalline. Sl. sol. boiling ether.

Thioglycerin $C_3H_8O_2S$ *i.e.* $C_3H_5(OH)_2(SH)$. Mol. w. 108. S.G. $^{14·4}$ 1·295. From chlorhydrin and boiling alcoholic KSH: the product is acidified and evaporated below 50° (Carius, *A.* 122, 72; 124, 222). Thick liquid; v. sl. sol.

water, insol. ether, miscible with alcohol. Reacts like mercaptan with metallic oxides and salts. Decomposed by heat into water H_2S and thiopyroglycide $C_6H_{12}O_3S$ an amorphous body, in ol. water and ether, sl. sol. boiling alcohol. Nitric acid oxidises thioglycerin to $C_3H_5(OH)_2SO_3H$. — $Hg(C_3H_7O_2S)_2$: [50°-60°]; white powder.—$Pb(C_3H_7O_2S)_2$: [c. 80°]; yellow pp.

Di-thio-glycerin $C_3H_8OS_2$ *i.e.* $C_3H_5(OH)(SH)_2$. Mol. w. 124. S.G $\frac{14\cdot4}{}$ 1·342. From *s*-dichlorhydrin and alcoholic KHS (Carius). Thick liquid, insol. ether, v. sl. sol. water, v. e. sol. alcohol. Split up on distillation into water, H_2S, and trithiopyroglycide $C_6H_{12}OS_3$. HNO_3 forms an acid $C_6H_{12}S_3O_{10}$.—$HgC_3H_6OS_2$ [c. 90°]. — $PbC_3H_6OS_2$: yellow powder.

Trithioglycerin $C_3H_8S_3$ *i.e.* $C_3H_5(SH)_3$. Mol. w. 140. S.G. $\frac{14\cdot4}{}$ 1·391. From *s*-trichloro-propane and alcoholic KSH (Carius). Liquid, m. sol. alcohol, insol. ether and water. Split up by heat into H_2S and dithioglycide $C_3H_5S(SH)$.—$Cu_3(C_3H_5S_3)_2$.—$Pb_3(C_3H_5S_3)_2$.—$Ag_3C_3H_5S_3$.

GLYCEROL *v.* GLYCERIN.

GLYCEROSE *v.* GLYCERIN, *Reaction* 6.

GLYCERYL. The trivalent radicle C_3H_5.

GLYCERYL BORATE $C_3H_5BO_3$. Formed by heating glycerin with B_2O_3 (Schiff a. Bechi, *Z.* 1866, 147). Glassy mass resolved by hot water into glycerin and boric acid. Not affected by boiling alcohol.

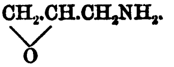
GLYCERYL CARLAMATE $C_3H_5(O.CO.NH_2)_3$. [215°]. From chloroformamide and glycerin (Gattermann, *A.* 244, 42). Needles (from HOAc). Insol. most solvents.

GLYCERYL CHLORIDE *v.* TRI-CHLORO-PROPANE.

GLYCERYL TRI-PHENYL-TRI-CARBAMATE $C_3H_5(O.CO.NHPh)_3$. *Phenyl-carbamic-glyceride.* Formed by heating glycerin (1 mol.) with phenyl cyanate (3 mols.) (Tessmer, *B.* 18, 968). White powder or fine needles. Sol. alcohol, acetone, ether, and chloroform, sl. sol. water and benzene. By heating with $Ba(OH)_2$ and water to 150° it yields glycerin, aniline, and $BaCO_3$.

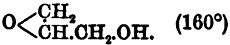
GLYCERYL SULPHOCYANIDE $C_6H_5N_3S_3$ *i.e.* $C_3H_5(SCy)_3$. [126°]. S. (alcohol) ·25 at 13°. From *s*-tri-bromo-propane and alcoholic KSCy at 100° (Henry, *B.* 2, 637). Small brittle needles (from alcohol). Insol. water, v. sol. boiling alcohol. Gives off HCy when heated.

GLYCIDAMINE C_3H_7NO *i.e.*

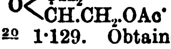

$CH_2.CH.CH_2NH_2$ with O bridging CH_2 and CH

Glyceramine. Formed, together with 'diamidohydrin' $C_3H_{10}N_2O$ by the action of alcoholic NH_3 on *s*-dichlorhydrin (Claus, *A.* 168, 29).—B HCl: crystals, ppd. by adding ether to the alcoholic solution; very hygroscopic.—$B'_2H_2PtCl_6$: transparent needles.

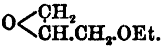
GLYCIC ACID *v.* GLUCIC ACID.

GLYCIDE $C_3H_6O_2$ *i.e.*  $O\!<\!\begin{matrix}CH_2\\CH.CH_2.OH\end{matrix}$. (160°) (B.); (157°) (H.). S.G. ^{0} 1·165. Prepared by adding powdered caustic soda (but not potash) to an ethereal solution of its acetate (Breslauer, *J. pr.* [2] 20, 192; *cf.* Gegerfelt, *Bl.* [2] 23, 160). Obtained by the action of BaO (28 g.) upon chlorhydrin (48 g.), dissolved in ether (50 g.) (Hanriot, *C. R.* 88, 387). Mobile liquid, miscible with water, alcohol, and ether. Heated with water it forms glycerin. Reduces ammoniacal silver nitrate in the cold. In presence of glycerin it rapidly forms products of condensation. Dilute HNO_3 forms glycerin mononitrate. Distillation with $KHSO_4$ gives acrolein.

Acetyl derivative

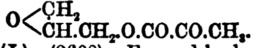

$O\!<\!\begin{matrix}CH_2\\CH.CH_2.OAc\end{matrix}$

(166°) (B.); (169°) (G.). S.G. $\frac{20}{}$ 1·129. Obtained by heating dry powdered potassic acetate with an equivalent quantity of epichlorhydrin over an oil bath, the temperature of which is slowly raised from 110° to 150°. After 20 hours the mass is extracted with ether and fractionated. An isomeric liquid (260°). S.G. $\frac{20}{}$ 1·204 is got as a by-product (Breslauer). Reduces ammoniacal $AgNO_3$.

Ethyl derivative  $O\!<\!\begin{matrix}CH_2\\CH.CH_2.OEt\end{matrix}$. (129°). S.G. $\frac{12}{}$ ·94. Formed by the action of KOH on the ethyl-chlorhydrin derived from ethyl allyl oxide and KOH (Reboul, *A. Ch.* [3] 60, 5; Henry, *B.* 5, 449). Liquid, sol. water. Readily combines with HCl. PCl_5 gives $C_3H_5Cl_2(OEt)$.

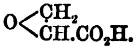
Isoamyl derivative $C_3H_5O_2.C_5H_{11}$. (188°). S.G. $\frac{20}{}$ ·90. From isoamyl-chlorhydrin and KOH.

Pyruvyl derivative $C_6H_8O_4$ *i.e.*


$O\!<\!\begin{matrix}CH_2\\CH.CH_2.O.CO.CO.CH_3\end{matrix}$

(?) [82°] (E.); [78°] (J.). (260°). Formed by heating equi-molecular proportions of glycerin and glyceric acid at 120°, and crystallising the product from alcohol (Erhart, *M.* 6, 511). Formed also by distilling glycerin with tartaric acid (Jowanowitsch, *M.* 6, 467). Needles, sol. hot water, but slowly saponified thereby, sol. alcohol, benzene, and ether. Monoclinic: $a{:}b{:}c = 1\cdot48{:}1{:}\cdot77$; $\beta = 105°\ 33'$. Readily saponified by alkalis, alkaline earths, and their carbonates. Bromine forms di-bromo-pyruvic acid. Sodium-amalgam gives lactic acid. It forms the following salts which are derived from its hydrate $C_6H_{10}O_5$.—$KC_6H_9O_5$: silky needles. — $Ca(C_6H_9O_5)_2$ 2aq. — $Cu(C_6H_9O_5)_2$ 3aq: blue crusts.—$AgC_6H_9O_5$: needles.

GLYCIDIC ACID $C_3H_4O_3$ *i.e.*


$O\!<\!\begin{matrix}CH_2\\CH.CO_2H\end{matrix}$

Oxy-acrylic acid.

Formation.—1. By the action of alcoholic KOH on the α-chloro-β-oxy-propionic acid that is formed by the union of acrylic acid with HOCl (Melikoff, *B.* 13, 271; 14, 939).—2. In like manner from the isomeric β-chloro-α-oxy-propionic acid (Erlenmeyer, *B.* 13, 458).

Properties.—Liquid, miscible with water, alcohol, and ether. Slowly combines with water, becoming glyceric acid. Its calcium salt readily takes up water, changing to calcium glycerate. Conc. HClAq forms β-chloro-α-oxy-propionic acid.

Salts.—NH_4A'.—$KA'\ \frac{1}{2}$aq: small prisms.—$NaA'\ \frac{1}{2}$aq.—ZnA'_2 aq: amorphous.—AgA': trimetric tables; when its aqueous solution is boiled it deposits a silver mirror.

Ethyl ether EtA'. (162° uncor.). S.G. $\frac{21\cdot6}{4}$ 1·0933. From silver β-chloro-α-oxy-propionate and EtI (Melikoff, *B.* 21, 2052). Oil; smelling somewhat like malonic ether.

Homologues of glycidic acid *v.* METHYL-GLYCIDIC ACID.

GLYCINE *v.* GLYCOCOLL.

GLYCO-DI-AMIDO-BENZOIC ACID $C_{13}H_{16}N_2O_7$ *i.e.* $CO_2H.C_6H_3(NH)_2C_6H_{10}O_5$. Formed by heating a conc. aqueous solution of glucose (2 mols.) and diamido-benzoic acid (1 mol.) for some hours at 90° (Griess a. Harrow, *B.* 20, 2210). Small silvery plates (from water); v. sl. sol. cold water, nearly insol. alcohol and ether. Decomposed by melting. Not affected by boiling with aqueous HCl or baryta. Strongly dextrorotatory.—BaA'_2 (at 100°): amorphous.—HA'HCl: small plates; v. e. sol. water and alcohol.

GLYCOCHOLIC ACID $C_{26}H_{43}NO_6$. S. ·33 in the cold; ·83 at 100° (Strecker); ·033 at 20°; ·85 at 100° (Emich). S. (ether) ·093 at 20°; S. (benzene) ·009; S. ($CHCl_3$) ·011. $[\alpha]_D = 29·9°$ (Hoppe, *C. C.* 1859, 65). Occurs as sodium salt in the bile of animals, and in ox-bile it is accompanied by sodium taurocholate, cholesterin, pigments, &c. (Gmelin; Strecker, *A.* 65, 9; 67, 1; 70, 161, 166; Emich, *M.* 3, 326; *M.* 4, 108; Gorup-Besanez, *A.* 157, 286).

Preparation.—1. The pp. formed in fresh ox-bile by $Pb(OAc)_2$ is treated with boiling (85 p.c.) alcohol, and the hot filtrate decomposed by H_2S, mixed with water and set aside to crystallise.—2. Fresh ox-bile is evaporated to dryness over the water-bath; the residue is extracted with cold alcohol, and the filtrate mixed with a little ether. After some time the liquid is decanted from the sticky deposit, and more ether is added when the mixed sodium salts (Plattner's 'crystallised bile') slowly deposit. They are dissolved in water and dilute H_2SO_4 added, whereupon glycocholic acid slowly crystallises.—3. The readiest way of obtaining glycocholic acid consists in covering fresh bile in a tall cylinder with a layer of ether, and adding 2 c.c. of conc. HClAq for every 50 c.c. of the bile. The whole then usually solidifies after a while to a crystalline pulp of glycocholic acid, which may be re-crystallised from water (Hüfner, *J. pr.* [2] 10, 267). In this experiment the bile of castrated oxen and of calves does not crystallise; of other oxen it always crystallises; the bile of cows usually crystallises (Hüfner, *J. pr.* [2] 19, 302). Bile which when mixed with ether and HCl produces a crystalline pp. of glycocholic acid, contains in 100 pts. of mixed taurocholic and glycocholic acids from 71 to 88 pts. of the latter acid, while bile which does not produce such crystallisation contains only from 47 to 57 pts. of glycocholic acid to 53 and 43 pts. of taurocholic acid respectively (G. Hüfner, *J. pr.* [2] 25, 97). Nevertheless it cannot be held that taurocholic acid hinders the crystallisation of glycocholic acid, because a solution containing even 7 pts. of pure sodic taurocholate to 1 pt. of pure sodic glycocholate gives crystallisation when treated with HCl and ether. The cause of non-crystallisation is therefore not yet explained (H.).—4. According to Marshall (*H.* 11, 233), the quickest method of obtaining glycocholic acid in colourless crystals is as follows:—A drop of hydrochloric acid is added to fresh bile; the mixture shaken and filtered; ethyl ether and hydrochloric acid are then added to the filtrate; the mixture shaken and allowed to remain. The crystals formed are collected on a filter, washed with water holding hydrochloric acid and ether in solution, and dried in the air. By re-crystallisation they are obtained perfectly colourless.

Properties.—Bulky groups of slender needles. V. sl. sol. water, v. e. sol. alcohol, v. sl. sol. other solvents. Its aqueous solution has a sweet and slightly bitter taste. It reddens litmus. It is readily soluble in ammonia, aqueous alkalis, and baryta-water; the addition of acids to these solutions reppts. the acids in a resinous form which slowly becomes crystalline; this change is rapidly brought about by ether. The free acid and its salts are dextrorotatory. It is antiseptic. By heating above 140° it is converted into glycocholonic acid $C_{26}H_{41}NO_5$. With sugar and conc. H_2SO_4 it gives on warming the crimson colour characteristic of Pettenkofer's test (*v.* BILE). Solutions of glycocholic acid are not ppd. by gelatin (Maly a. Emich, *M.* 6, 95).

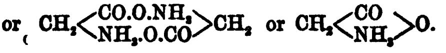
Reactions.—1. Boiling aqueous KOH splits it up into glycocoll and cholic acid $C_{24}H_{40}O_5$. Boiling *baryta-water* effects the like hydrolysis.—2. Conc. HClAq and conc. H_2SO_4 dissolve it in the cold, and water reppts. it from these solutions, but the boiling acids deposit oily drops of glycocholonic acid which solidify after a while.—3. Boiling dilute HCl forms choloïdic acid, dyslysin, and glycocoll.—4. *Nitrous acid vapour* passed into its solution forms 'chologlycollic acid' $C_{20}H_{42}O_7$ (Lang, *Bl.* [2] 25, 180). This acid is amorphous, but forms a crystalline barium salt $Ba(C_{20}H_{41}O_7)_2$ 3aq.—5. When mixed with HOAc and H_2SO_4 and heated it forms an orange colouring matter possibly related to the bile-pigments (Michailoff, *B.* 17, 444, *Ref.*; *J. R.* 1884 [1] 584).—6. By heating with alcoholic NH_3 at 170° for 24 hours there is formed a substance $C_{24}H_{41}NO_4$, which on evaporation crystallises in long silky deliquescent needles [125°] (Pellizzari, *C. C.* 1888, 1350).

Salts.—Solutions of the alkaline salts lather like soap. All the glycocholates are soluble in alcohol, those of the alkalis and alkaline earths dissolve easily in water, the rest are sparingly soluble and may be obtained by precipitation.—NaA' (at 100°). S. (alcohol) 1·5. The alcoholic solution deposits crystals when very slowly evaporated in a flask. Dry ether added to its alcoholic solution throws it down in an amorphous state, but if the ether is wet it becomes crystalline (Städeler, *J. pr.* 72, 257).—BaA'_2 (at 100°) amorphous, S. 16·2 at 15°.—PbA'_2 (at 100°).

Ethyl ether $C_{26}H_{42}EtNO_6$. S.G. ·901. Prepared by saturating an alcoholic solution of the acid with HCl and heating in sealed tubes (Springer, *Am.* 1, 181). Slowly saponified by water.

Paraglycocholic acid $C_{26}H_{43}NO_6$. [184°]. When glycocholic acid is ppd. by H_2SO_4 from a solution of its Na salt, and the pp. is boiled with water paraglycocholic acid remains undissolved. Alcohol and boiling alkalis reconvert it into the ordinary modification.

GLYCOCOLL $C_2H_5NO_2$ *i.e.* $CH_2(NH_2).CO_2H$



or $CH_2<\begin{matrix}CO.O.NH_2\\NH_2.O.CO\end{matrix}>CH_2$ or $CH_2<\begin{matrix}CO\\NH_3\end{matrix}>O$.

Amido-acetic acid. Mol. w. 75. (232°–236° cor.). S. 23. S.G. 1·161. H. C. 228,000 (Stohmann, *J. pr.* [2] 31, 285). Occurs in the mussel *Pecten irradians* (Chittenden, *A.* 178, 273).

Formation.—1. Discovered by Braconnot (*A. Ch.* [2] 13, 114), who obtained it by boiling gelatin with dilute H_2SO_4.—2. Formed also by boiling gelatin with potash or baryta (Mulder, *J. pr.* 16, 290).—3. By boiling hippuric acid with dilute HCl (Dessaignes, *A.* [3] 17, 50; Kraut a. Hartmann, *A.* 133, 99).—4. By decomposing glycocholic or hyoglycocholic acid with dilute acids or alkalis (Strecker, *A.* 67, 25; 70, 188).—5. From bromo-acetic acid and NH_3 (Perkin a. Duppa, *A.* 108, 112).—6. Together with CO_2 and NH_3 by heating uric acid with conc. HIAq at 165° (Strecker, *Z.* [2] 4, 215).—7. By the action of aqueous HI on hydantoic acid (Menschutkin, *A.* 153, 105).—8. From nitroso-thio-hydantoin or nitroso-thio-glycollic acid and HI (Andreasch, *M.* 6, 827).—9. From glyoxal by successive treatment with ammonium cyanide and dilute H_2SO_4 (Lubavine, *Bl.* [2] 38, 379).—10. By passing cyanogen into boiling HIAq (S.G. 1·96) (Emmerling, *B.* 6, 1351).—11. From cyanoformic ether, zinc, and HCl (Wallach, *A.* 184, 13).—12. To the extent of about 7·5 p.c. by boiling silk with dilute H_2SO_4 (Weyl, *B.* 21, 1531).

Preparation.—1. Hippuric acid 500 g. is boiled with conc. HCl for 12 hours. The benzoic acid formed is removed by filtration and extraction with ether, after which the liquor containing the hydrochloride of glycocoll is evaporated until crystallisation sets in. The salt is washed with absolute alcohol. The yield is 90 p.c. (Curtius a. Goebel, *J. pr.* [2] 37, 157).—2. Hippuric acid (1,200 g.) is boiled for 12 hours with H_2SO_4 (1,600 g.) diluted with water (3,200 g.). The product is allowed 24 hours to cool, it is then filtered. The filtrate is evaporated and shaken three times with ether to remove the last traces of benzoic acid. The liquid is diluted and neutralised with baryta (free from iron). The liquid is decanted from $BaSO_4$ and evaporated. Some of the dissolved barium can be removed by CO_2. The glycocoll crystallises out from the evaporated filtrate (T. Curtius, *J. pr.* [2] 26, 153).—3. By heating chloro-acetic acid (1 pt.) with solid ammonium carbonate (3 pts.) to 70° and finally to 130° (Nencki).—4. Chloro-acetic acid (50 g.) and sodium carbonate (53 g.) are warmed with excess of aqueous ammonia. After boiling for 7 hours hydrochloric acid is added and the liquid evaporated, ppd. with alcohol and filtered. The filtrate is digested with $Cu(HO)_2$, warmed, filtered, and treated with alcohol, and then with hydrogen sulphide (Mauthner a. Suida, *M.* 9, 728).—5. By heating phthaloxyl-amido-acetic acid $CO_2H.C_6H_4.CO.NH.CH_2.CO_2H$ with double its weight of 20 p.c. pure HCl, diluting with water, filtering, evaporating, and treating with ice-cold water, which leaves behind phthalic acid. On evaporating and washing with absolute alcohol, hydrochloride of glycocoll remains as a snow-white crystalline powder (S. Gabriel a. K. Kroseberg, *B.* 22, 428).

Properties. — Monoclinic tablets; $a:b:c = 1:1{\cdot}857:2{\cdot}204$; $\beta = 68° 20'$ (Schabus). Slight impurities change the crystalline form remarkably: traces of NaOH or TlOH cause it to form rhombohedra, while traces of baryta induce the formation of very long thin prisms (Curtius). Glycocoll is inactive. It has a sweet taste. Sl. sol. water, insol. ether and alcohol. Neutral to litmus. It prevents the ppn. of cupric hydroxide from its sulphate by potash (Horsford, *A.* 60, 1). $FeCl_3$ gives a deep-red colour (Engel, *Fr.* 15, 344).

Reactions.—1. Distillation with BaO gives methylamine and $BaCO_3$. Solid KOH acts in like manner but NH_3, hydrogen, and potassium oxalate are also formed (Cahours, *A. Ch.* [3] 53, 322; *A.* 109, 29).—2. Dilute H_2SO_4 and MnO_2 give off CO_2 and HCy.—3. *Nitrous acid gas* converts it into glycollic acid (Socoloff a. Strecker, *A.* 80, 18; Dessaignes, *C. R.* 38, 44).—4. When heated with *benzoic acid* in sealed tubes, hippuric acid is formed (Dessaignes, *J. Ph.* [3] 32, 44). Hippuric acid is also formed by treating zinc or silver glycocoll with BzCl (Dessaignes, *C. R.* 37, 251).—5. *Cyanamide* forms glycocyamine $C_3H_7N_3O_2$ (Strecker, *C. R.* 52, 1212).—6. *Phenyl-cyanamide* in ammoniacal solution mixed with an alcoholic solution of glycocoll forms on standing crystalline grains of $C_9H_{11}N_3O_2$ (Berger, *B.* 13, 992).—7. With *sodium hypobromite* nitrogen is evolved (Denigès, *C. R.* 107, 662).—8. When a concentrated solution of glycocoll is mixed with NaOH and *phenyl-acetic chloride* a reaction takes place and on acidifying phenyl-aceturic acid separates. Its ether $C_{10}H_{10}NO_3Et$ crystallises in broad prisms [79°].—9. When *benzoic aldehyde* is added to an aqueous solution of glycocoll saturated with SO_2 there is formed syrupy $C_9H_{13}NSO_6$ which slowly solidifies over H_2SO_4 (Schiff, *A.* 210, 125). *Œnanthol* forms a similar compound $C_7H_{14}OC_2H_5NO_2H_2SO_3$.—10. Heated with *cholic acid* at 200° for 20 hours there is formed a product whence NaOH ppts. amorphous glycodyslysin $C_{26}H_{29}NO_4$ (Lang, *Bl.* [2] 25, 180).—11. *Chloroform* and KOH form isocyano-acetic acid $C{:}N.CH_2.CO_2H$ (Calmels, *Bl.* [2] 42, 266).—12. *Guanidine carbonate* forms the compound $C_2H_5NO_2(CH_5N_3)_2CO_2aq$ (Nencki a. Sieber, *J. pr.* [2] 17, 480).—13. *Urea* (10 pts.) at 230° forms uric acid (Horbaczewski, *B.* 15, 2678).

Salts.—The fact that glycocoll only forms salts with such metals as can displace the hydrogen of amidogen tends to show that the salts have the formula $CH_2(NHR)CO_2H$, and not $CH_2(NH_2)CO_2R$. Thus it forms no salts with alkalis, and probably none with alkaline earths.

Barium salt.—If excess of baryta be added to glycocoll sulphate and the solution be filtered the liquid may perhaps contain glycocoll-barium, but on adding alcohol a pp. is got, which contains variable amounts of glycocoll and baryta. If this pp. be recrystallised from alcohol it becomes pure glycocoll. Hence glycocoll-barium is very unstable, if indeed it exists (Curtius, *J. pr.* [2] 26, 151).

Zinc salt $C_2H_4NO_2Zn$ aq. Partially decomposed by hot water. Boiling Na_2CO_3 removes one-third of the zinc.

Silver salt AgA′. Prepared by heating silver oxide (38 g.) nearly to boiling with a solution of glycocoll (100 g.). The hot liquid is filtered and allowed to cool in the dark. After an hour the liquid is poured off from the silver glycocoll and heated with the remaining silver oxide. This process is repeated until the quantity of silver glycocoll that separates on cooling begins to decrease when a fresh quantity of silver oxide (38 g.) is added to that which still remains, and the process is continued till all the silver oxide is either used up or reduced to silver. Yield 75 p.c. (Curtius, *J. pr.* [2] 26, 165). Crystallises in tablets. Turns grey in daylight. It is not hygroscopic. It is strongly alkaline. It decomposes at 100°. Warmed with a mixture of benzene and benzoyl chloride it forms silver chloride and the three following acids: (1) Hippuric acid (Dessaignes, *C. R.* 37, 251); (2) an acid $C_{11}H_{12}N_2O_3$: [207°], which when boiled with dilute acids gives benzoic acid and *two* molecules of glycocoll, and hence it may perhaps be written $Ph.CO.NH.CH_2.CO.NH.CH_2.CO_2H$; (3) an acid $C_{10}H_{12}N_3O_4$, which blackens at 240° without melting, but with acids gives also benzoic acid and glycocoll on boiling (T. Curtius, *J. pr.* 132, 239). Silver glycocoll is converted by EtI into $NEt_3I.CH_2.CO_2Et$.—AgA'HOEt. Obtained by ppg. a solution of silver glycocoll by alcohol.

Other salts.—PdA'_2: yellow needles (Drechsel, *J. pr.* [2] 20, 475).—CdA'_2aq: silky foliated crystals.—CuA'_2aq: blue needles. S. ·6 at 15°.—PbA'_2aq: needles.—HgA'_2aq: small crystals.

Salts with acids.—HA'HCl: deliquescent crystals, v. e. sol. water, sl. sol. alcohol; has an acid, slightly astringent taste.—$H_2A'_2HCl$: trimetric crystals; *a*:*b*:*c* = 1 : 1·1108 : ·3091.—$H_2A'_2H_2PtCl_6$.—$HA'HNO_3$: [145°]. Decomposed by fusion (Franchimont, *R. T. C.* 2, 339). Trimetric crystals; *a*:*b*:*c* = 1:3·412 : 2·969 (Nicklès, *Compt. Chim.* 1849, 256); = ·0687 : ·750 : 1 (Loschmidt, *Sitz. W.* 51 [2] 386). According to Horsford they are monoclinic.—$H_2A'_2HNO_3$.—$H_2A'_2H_2SO_4$. Large prisms, permanent in the air; sol. water, insol. alcohol and ether. According to Nicklès the crystals are trimetric; *a*:*b*:*c* = 1 : ·424 : ·321.—HA'HOAc $1\frac{1}{2}$aq: crystallises from water.—$H_2A'_2H_2C_2O_4$: trimetric crystals; *a*:*b*:*c* = 1 : 3·072 : 2·792 (N.).

Combinations with both acids and bases.—KA'HCl.—$BaA'_2H_2Cl_2$: trimetric prisms.—$KA'HNO_3$: needles (Boussingault, *A.* 39, 310).—$CuA'_2Cu(NO_3)_2$ 2aq: blue needles.—$AgA'HNO_3$: needles.—$KHA'_2H_2SO_4$: prisms.

Acetyl derivative v. ACETURIC ACID.

Benzoyl derivative v. HIPPURIC ACID.

Salicyl derivative v. OXY-BENZOIC ACID.

Methyl ether $NH_2.CH_2.CO_2Me$. (54°) at 50 mm. Obtained by suspending its hydrochloride in ether, shaking with the theoretical amount of Ag_2O, evaporating the filtrate, drying over BaO and fractionally distilling (Curtius a. Goebel, *J. pr.* [2] 37, 165). Liquid, miscible with all ordinary menstrua; boils with decomposition at 130°. It forms a copper salt crystallising in blue needles, v. sol. water. $Cu(NH.CH_2.CO_2Me)_2$aq. Hydrochloride $NH_3Cl.CH_2.CO_2Me$. [175°]. Formed by passing dry gaseous HCl through methyl alcohol containing glycocoll hydrochloride in suspension until solution takes place (Curtius a. Goebel, *J. pr.* [2] 37, 159). Prisms, v. sol. cold alcohol. Yields ethylamine when distilled with Na_2CO_3. Its platinochloride is v. sol. alcohol and water.

Acetyl derivative of the methyl ether v. ACETURIC ACID.

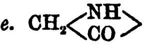
Ethyl ether $NH_2.CH_2.CO_2Et$. (149°) at 748 mm.; (65°) at 40 mm. V.D. 3·47 (calc. 3·57). Formed by treating its hydrochloride in ethereal solution with Ag_2O as in the preceding case (G. a. C.). Formed also from bromo-acetic ether by treatment with silver nitrite and reduction of the resulting nitro-acetic ether (De Forcrand, *C. R.* 88, 974). Colourless liquid, miscible with water, alcohol, ether, benzene, $CHCl_3$, and petroleum-ether. Somewhat volatile with steam. Absorbs CO_2. Does not solidify at −20°. Gives *n*-propylamine when distilled with Na_2CO_3. Its copper salt $Cu(NH.CH_2.CO_2Et)_2$ 2aq crystallises in blue plates, v. sol. water. Hydrochloride $NH_3Cl.CH_2.CO_2Et$. [144°]. Formed by passing dry HCl into alcohol containing glycocoll hydrochloride in suspension until solution occurs (G. a. C.). Long needles; may be sublimed. Its platinochloride forms needles [212°]. Hydroiodide $NH_3I.CH_2.CO_2Et$. Formed by heating glycocoll with alcohol and EtI or even MeI at 120° (Schilling, *A.* 127, 97; Kraut, *A.* 177, 267). Trimetric crystals. With Ag_2O it gives glycocoll, alcohol, and AgI.—Nitrate $NH_3(NO_3)CH_2CO_2Et$. Crystals (Curtius, *B.* 17, 953).

Acetyl derivative of the ethyl ether v. ACETURIC ACID.

Allyl ether. Hydrochloride $NH_3Cl.CH_2.CO_2C_3H_5$. [170°–180°]. Prepared by suspending glycocoll hydrochloride in allyl alcohol and passing HCl until a solution is obtained (C. a. G.). Thin plates, m. sol. cold alcohol.

Isoamyl ether. Hydrochloride $NH_3Cl.CH_2.CO_2C_5H_{11}$. From glycocoll, isoamyl alcohol, and HCl. Syrup.

Phenyl ether $NH_2.CH_2.CO_2C_6H_5$. From phenyl chloro-acetate and alcoholic NH_3 at 140°. Needles, sol. water, v. sl. sol. alcohol and ether (Prevost, *J. pr.* [2] 4, 379).



Anhydride C_2H_3NO *i.e.* $CH_2<\begin{matrix}NH\\CO\end{matrix}>$ or $CH_2<\begin{matrix}NH.CO\\CO.NH\end{matrix}>CH_2$. [275°]. Prepared by decomposing an aqueous solution of the hydrochloride of glycocoll ethyl or methyl ether with silver oxide and extracting the mixture of silver chloride and anhydride with hot water, by which the latter is dissolved out and crystallises on cooling (Curtius a. Goebel, *J. pr.* [2] 37, 173). Plates. V. sol. hot water and dilute alcohol. Neutral to litmus. It does not combine with ammonia and the alkali metals, but forms salts with silver (C_2H_2AgNO) and copper. It forms a hydrochloride crystallising in long needles [130°], converted by boiling water into glycocoll hydrochloride.—Platinochloride $B'_4(HCl)_2PtCl_4$ 3aq. Large orange-yellow crystals, m. sol. water, sl. sol. alcohol.

Amide $NH_2.CH_2.CO.NH_2$. *Amido-acetamide.* Formed in small quantity by heating glycocoll with alcoholic NH_3 at 160°. It is also one of the products of the action of alcoholic NH_3 on chloro-acetic ether (Heintz, *A.* 148, 190; 150, 67). Obtained from its hydrochloride by treatment with Ag_2O. Solid; v. e. sol. water; alkaline in reaction. Decomposed by boiling water into NH_3 and glycocoll.—B'HCl: monoclinic needles; v. e. sol. water, sl. sol. alcohol.—$B'_2H_2PtCl_6$.

Ethyl-glycocoll v. ETHYL-AMIDO-ACETIC ACID.

Phenyl-glycocoll v. PHENYL-AMIDO-ACETIC ACID.

Nitro-phenyl-glycocoll v. NITRO-PHENYL-AMIDO-ACETIC ACID.

Sulpho-phenyl-glycocoll v. SULPHO-PHENYL-AMIDO-ACETIC ACID.

Nitro-tolyl-glycocoll *v.* NITRO-TOLYL-AMIDO-ACETIC ACID.

GLYCOCOLONIC ACID $C_{26}H_{41}NO_5$. A product of the action of conc. HClAq on glycocholic acid (Strecker, *A.* 67, 26; 70, 166). Formed also by heating glycocholic acid above 140°. Needles (from alcohol). Insol. water and ether, v. sol. alcohol. Decomposed by boiling HClAq into glycocoll and cholic acid. NaA′: crystals (from alcohol) (Mulder, *J.* 1847-48, 907).

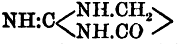
GLYCOCYAMINE $C_3H_7N_3O_2$ *i.e.* $NH:C(NH_2).NH.CH_2.CO_2H$. *Guanido-acetic acid.* Mol. w. 117. S. ·8 (Strecker), ·44 (Nencki).

Formation.—1. By adding a few drops of ammonia to an aqueous solution of glycocoll mixed with cyanamide (Strecker, *C. R.* 52, 1212). 2. By heating an aqueous solution containing glycocoll and guanidine carbonate, glycocyamine and ammonic carbonate are formed (Nencki a. Sieber, *J. pr.* [2] 17, 477); the reaction taking place as follows: $2C_2H_5NO_2 + (CH_5N_3)_2H_2CO_3 = 2C_3H_7N_3O_2 + (NH_4)_2H_2CO_3$. Probably the guanidine first breaks up into cyanamide and ammonia.

Properties.—Transparent needles. Sl. sol. cold, v. sol. hot, water; insol. alcohol. Boiled with cupric acetate it gives microscopic crystals of $Cu(C_3H_6N_3O_2)_2$.

Salts.—HA′HCl: prisms; v. sol. water.—$H_2A'_2H_2PtCl_6$ 3aq.

Glycocyamidine $C_3H_5N_3O$ *i.e.*



$$NH:C\left<\begin{matrix}NH.CH_2\\NH.CO\end{matrix}\right>$$

The hydrochloride is obtained by heating glycocyamine hydrochloride to 160° (Strecker). The base may be liberated by boiling this salt with lead hydroxide and water. Laminæ; v. e. sol. water. Has an alkaline reaction. It forms a compound with $ZnCl_2$ crystallising in needles resembling the corresponding salt of creatinin.—B′HCl: v. sol. water.—$B'_2H_2PtCl_6$ 2aq: needles.

Reference.—BENZ-GLYCOCYAMIDINE.

GLYCODRUPOSE *v.* CELLULOSE.

GLYCODYSLYSIN $C_{26}H_{39}NO_4$. An amorphous powder formed by heating glycocoll with cholic acid at 195° (Lang, *Bl.* [2] 25, 182). Sl. sol. water, v. sol. ether, v. e. sol. alcohol. Not attacked by alcoholic KOH. Boiling HClAq forms glycocoll.

GLYCOGEN $C_6H_{10}O_5$.

Occurrence.—In the liver and in the placenta, entering largely into the constitution of most of the tissues of the embryo (Cl. Bernard, *C. R.* 41, 461; 44, 578, 1325; 48, 77, 763, 884; Sanson, *C. R.* 44, 1159, 1323; 45, 140, 343; Schiff, *C. R.* 48, 880; E. Pelouze, *C. R.* 44, 1321; Bonnet, *C. R.* 45, 139, 573; Kekulé, *C. C.* 1858, 300; Poggiale, *J. Ph.* [3] 34, 99; Harley, *Pr.* 10, 289; Pavy, *P. M.* [4] 17, 142; *Pr.* 10, 528; 11, 90; Gorup-Besanez, *A.* 118, 227; McDonnell, *Pr.* 12, 476; Wittich, *Fr.* 14, 227; Aldehoff, *Z. B.* 25, 137; Manché, *Z. B.* 25, 163; Chandelon, *Pf.* 13, 626; Schmelz, *Z. B.* 24, 180). As much as 11 p.c. has been found in the liver of new-born puppies (Demant, *H.* 11, 142). Occurs also in blood, muscle, spleen, kidneys, pancreas, and brain (Pavy, *Pr.* 32, 418), and in the white and yolk of egg. Glycogen is uniformly distributed throughout the liver, but in the muscles of the heart, where it also occurs, it is unevenly distributed (Cramer, *Zeit. Biol.* 24, 67). Occurs in the urine in diabetes mellitus (Leube, *C. C.* 1888, 1278). In vesicular cells of the connective tissue of mollusca, such as oysters (Bizio, *C. R.* 62, 675; 65, 175; Blundstone, *Pr.* 38, 442). In the cockroach (*Blatta orientalis*), and in *Bombyx mori* (a butterfly) and its chrysalis (Anderlini, *C. C.* 1888, 451). It is present in a large number of fungi, where it seems to take the place of the starch of higher plants (Errera, *C. C.* 1888, 252). It is present in beer-yeast (Errera, *C. R.* 101, 253; Laurent, *C. C.* 1888, 252). Found in ciliated infusoria (Maupas, *C. R.* 101, 1504). When the following substances are introduced into the systems of starved dogs or rabbits no appreciable quantities of glycogen are found in the liver: inosite, mannite, quercite, erythrite, and fats. But glucose, milk-sugar, cane-sugar, lævulose, inulin, glycerin, gelatin, and proteïds promote the formation of glycogen. It is not clear whether the glycogen is directly formed from these substances or whether their presence promotes its formation from some other source, or hinders its destruction when formed (Von Mering, *Pf.* 14, 274; *cf.* Forster, *N. Rep. Pharm.* 25, 733; Wolfberg, *Zeit. f. Biol.* 12, 266; Seegen, *Pf.* 40, 48; Chittenden a. Lambert, *Dissertation* 1885). Asparagine, glycocoll, and, above all, ammonium carbonate, when given to rabbits with a carbohydrate diet greatly increase the amount of glycogen in the liver (Röhmann, *Pf.* 39, 21).

Preparation.—1. Glycogen is best obtained pure by Brücke's method (*Sitz. W.* 63 [2] 214), which readily separates all proteïds from it. A solution of potassio-mercuric iodide is prepared by precipitating mercuric chloride with potassium iodide, washing the precipitate and then saturating a boiling solution of potassium iodide with it. A watery solution of glycogen, mixed with albuminous matters, is prepared by cutting a perfectly fresh liver into pieces about the size of a hazel-nut, and throwing them into boiling water for a couple of minutes, so as to destroy the liver ferment, which would otherwise convert the glycogen into sugar; the pieces are then bruised in a mortar and extracted with boiling water, and the solution is filtered. As soon as the filtrate is cold it is treated alternately with hydrochloric acid and the potassio-mercuric iodide solution as long as these agents produce any precipitate, and after standing for five minutes the solution is again filtered. Alcohol is then added until about 60 p.c. of absolute alcohol is present in the liquid: this throws down the glycogen alone, but more alcohol precipitates other bodies with it. The precipitate is collected on a filter, washed first with weak, then with 90 p.c. alcohol, and finally with ether, and is then transferred to a tile to dry. Glycogen is thus obtained as a snow-white amorphous powder; if impure or not quite dry, it forms a semi-transparent brittle mass.—2. The boiling aqueous decoction of liver is treated with $ZnCl_2$; the filtrate is evaporated and mixed with dilute (60 p.c.) alcohol, acidified with HCl. The ppd. glycogen is washed with alcohol (Abeles, *J. Th.* 1881, 58; *Pf.* 24, 485).

Properties.—White mealy amorphous powder. According to Külz a. Bornträger (*Pf.* 24, 19) at 100° it is $(C_6H_{10}O_5)_6$aq. With water it forms an opalescent solution. On evaporating this solution the glycogen separates in films. Its aqueous solution is dextrorotatory $[\alpha]_D$ varying from 203° to 234° according to concentration (Külz, *Pf.* 24, 85; Landwehr, *Z.* 8, 171); but the polariscope may be used in its estimation (Cramer, *Z. B.* 24, 180). It is insol. alcohol. Its ppn. from aqueous solutions by alcohol is greatly promoted by the presence of NaCl and other salts (Külz, *B.* 15, 1300). Charcoal removes it from its aqueous solution. Iodine colours its aqueous solution red. Glycogen does not reduce Fehling's solution. Glycogen dissolves in cold conc. H_2SO_4 forming an amorphous acid. With baryta-water it gives a pp. of $BaO(C_6H_{10}O_5)_3$, while lead subacetate forms $PbO(C_6H_{10}O_5)_2$.

Estimation.—The substance is extracted with hot dilute KOH, the proteids are ppd. from the solution by HCl and potassio-mercuric iodide, and the glycogen is then ppd. by alcohol, dried, and weighed (Külz, *Z. B.* 22, 161).

Reactions.—1. *Diastase* and *saliva* transform it into maltose, a little glucose, and an achroo-dextrin (Musculus a. Mering, *H.* 2, 413; Siegen, *C. C.* 1877, 8). It is not changed to sugar, to any significant extent, by contact with blood (Pavy, *Pr.* 32, 418). Boiling dilute mineral acids convert it into glucose (Külz a. Bornträger, *Pf.* 24, 28).—2. Does not ferment with *yeast.*—3. Boiling dilute HNO_3 forms oxalic acid.—4. *Bromine* followed by Ag_2O forms glycogenic acid. 5. Cold conc. HNO_3 forms amorphous 'nitroglycogen' $C_{12}H_{19}(NO_2)O_{10}$, insol. water, alcohol, and ether, sol. alkalis and dilute HCl (Lustgarten, *M.* 2, 634).—6. A mixture of fuming HNO_3 and H_2SO_4 forms 'di-nitro-glycogen' $C_6H_8(NO_2)_2O_5$, a white powder, insol. water, alcohol, ether, alkalis, and dilute acids, which explodes at 80° to 90°. It is converted by ammonium sulphide into a dextrin which has but slight power of reducing Fehling's solution, and is dextrorotatory $[\alpha]_D = 194$ at 27° (Lustgarten). 7. Ac_2O at 155° forms an amorphous tri-acetyl-derivative $C_6H_7Ac_3O_5$, insol. water, alcohol, and ether (Schutzenberger, *A.* 160, 80).

Achroo-glycogen $C_6H_{10}O_5$. Obtained from snail's mucin, by treating with 5 to 10 p.c. aqueous KOH, separating proteïds by potassio-mercuric iodide, filtering, and ppg. the achroo-glycogen by alcohol (Landwehr, *Z.* 6, 74). Amorphous white tasteless solid, v. sol. water, forming a strongly opalescent solution. It does not reduce Fehling's solution. By treatment with saliva, diastase, or boiling dilute acids it is converted into dextrin and glucose. It differs from glycogen in giving no colour with iodine.

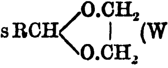
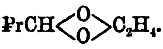
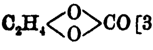
GLYCOGENIC ACID $C_6H_{12}O_7$. Formed by treating an aqueous solution of glycogen at 100° with bromine, and then adding Ag_2O (Chittenden, *A.* 182, 206). Very acid syrup. Is perhaps identical with gluconic acid.—CaA'_2: minute needles; sl. sol. cold water.—BaA'_2 3aq: prisms. —$Pb_2C_6H_8O_7$.—CoA'_2 2aq.

GLYCOL $C_2H_6O_2$ *i.e.* $CH_2(OH).CH_2(OH)$. *Ethylene alcohol.* Mol. w. 62. [−11·5°] (Bouchardat, *C. R.* 100, 452). (198° cor.). S.G. $\frac{15}{15}$ 1·1168; $\frac{25}{25}$ 1·1121 (Perkin, *C. J.* 45, 504); $\frac{20}{4}$ 1·1072 (Brühl). M.M. 2·943 at 15·1° (P.). $\mu_\beta = 1·4325$. $R_\infty = 23·32$. H.F.p. 100,890 (*Th.*). H.F.v. 99,150. S.V. 65·6 (Ramsay).

Formation.—1. From ethylene iodide by distilling with silver acetate and saponifying the resulting diacetate $C_2H_4(OAc)_2$ with solid KOH (Wurtz, *C. R.* 43, 199; *A. Ch.* [3] 55, 400; *A.* 100, 110; *Suppl.* 1, 85).—2. By heating for 2 days in a sealed tube at 100° a mixture of ethylene bromide (60 g.) with potassium acetate (60 g.) and (85 p.c.) alcohol (120 g.), and saponifying the resulting mono-acetate $CH_2(OH).CH_2OAc$ with potash or baryta (Atkinson, *P.M.* [4] 16, 433). Debus (*A.* 110, 316) recommends saponifying the mono-acetate with water in sealed tubes at 100°. By heating a mixture of ethylene bromide (195 g.), KOAc (102 g.), and dilute alcohol (200 g. of S.G. ·82), Demole (*A.* 173, 117) obtained glycol and acetic ether. From 600 g. ethylene bromide Erlenmeyer (*A.* 192, 246) obtained 125 g. glycol.—3. Together with poly-ethylenic glycols by heating ethylene oxide with water (Wurtz).—4. From ethylene chloro-iodide and moist Ag_2O at 160° to 200° (Maxwell Simpson, *A. Suppl.* 6, 253).—5. Together with NMe_3 by boiling a conc. aqueous solution of neurine (Wurtz, *A. Suppl.* 6, 200).—6. By heating ethylene bromide (1 pt.) with water (12 pts.) and PbO at 150° (Eltekoff, *B.* 6, 558).—7. From ethylene bromide (55½ pts.), water (180 pts.), and Ag_2CO_3 (41 pts.). Ag_2O and Ag_2SO_4 used instead of Ag_2CO_3 do not give glycol (Beilstein a. Wiegand, *B.* 15, 1368).

Preparation.—1. Ethylene bromide (188 g.) is boiled with water (1000 g.) containing K_2CO_3 (138 g.) in solution in a flask with inverted condenser. A large quantity of vinyl bromide escapes. As soon as all the ethylene bromide has disappeared the liquid is evaporated to dryness, and the glycol separated from the KBr by solution in alcohol. The alcohol is then distilled, when the glycol (13 g.) passes over at 198° (Zeller a. Hüfner, *J. pr.* [2] 10, 270). In this process Na_2CO_3 (106 g.) may be used instead of K_2CO_3, whereby the yield may be increased (to 35 g.), although the product is not so pure (Stempnewsky, *A.* 192, 242). $BaCO_3$ used instead of K_2CO_3 yields no glycol.—2. By heating ethylene bromide (1 pt.) with water (26 pts.) for 130 hours in sealed tubes at 100°; the yield being 60 p.c. (Niederist, *A.* 196, 354).

Properties.—Colourless liquid, with sweet taste, but no smell. Miscible with water and alcohol; sl. sol. ether. It dissolves KOH, $Ca(OH)_2$, $CaCl_2$, NaCl, $ZnCl_2$, $SbCl_3$, and $HgCl_2$. In a freezing mixture it sometimes solidifies to a mass of crystals.

Reactions.—1. When dropped upon *platinum black*, CO_2 is given off and the metal may even become incandescent. If in this experiment the glycol be diluted with water and the air with CO_2, glycollic acid is produced by the oxidation. 2. Cold dilute *nitric acid* forms glycollic acid, at higher temperatures it forms oxalic acid. When glycol diluted with four times its volume of water is placed in a tall vessel and strong nitric acid is introduced so as to form a layer at the bottom, and the whole is kept for some time at 30°, there is formed glycollic acid, glyoxylic acid, and perhaps also glyoxal (Debus, *A.* 110, 316).—3. *Caustic potash* at 250° forms oxalic acid with evolution of hydrogen.—4. By heating with *zinc chloride* at 250° there is formed aldehyde and crotonic aldehyde (Bauer, *Rép. chim. pure*, 1860, 244).—5. By heating with a large quantity of *water* at 210° there is also formed aldehyde (Nevole, *Bl.* [2] 25, 289).—6. By heating with *acids* it yields ethers by displacement of one or both of its hydroxyls by acid residues (Lourenço, *A.* 111, 122).—7. PCl_5 gives ethylene chloride (Wurtz, *A.* 104, 174).—8. *Acetyl chloride* forms $CH_2Cl.CH_2OAc$.—9. By heating with *ammonium chloride* at 180°-190° for 8 hours there is formed tri-methyl-pyridine (collidine) $C_8H_{11}N$; the yield being 15 to 20 p.c. of the theoretical (Hofmann, *B.* 17, 1905).—10. Heated with fuming HCl in a sealed tube at 100° it forms ethylene chloride (Schorlemmer, *C. J.* 39, 143); but when saturated with HCl in an open vessel and then distilled the product is glycol chlorhydrin.—11. *Chlorine* forms oily $C_6H_{12}O_4$ (240°) and a crystalline chlorinated body [39°] (c. 200°) (A. Mitscherlich, *C. R.* 56, 188).—12. An aqueous solution of glycol acidulated with H_2SO_4 is converted by electrolysis into CO, oxygen, and CO_2, together with formic paraldehyde (tri-oxymethylene), formic, acetic, and glycollic acids, and a polymeride of formic aldehyde resembling glucose (Renard, *A. Ch.* [5] 17, 315).—13. By heating glycol (2 pts.) with *soda-lime* (5 pts.) at 250° there is formed an acid $C_{25}H_{48}O_4$ [103°] which may be crystallised from ligroïn and ether (Stürcke, *A.* 223, 300).—14. When heated with *aldehydes* RCHO, glycol forms ethylene derivatives of the ortho-aldehydes  $RCH\langle\begin{matrix}O.CH_2\\ |\\ O.CH_2\end{matrix}$ (Wurtz, *Rép. chim. pure*, 1862, 16; Lochert, *A. Ch.* [6] 16, 35). Thus isobutyric aldehyde gives  $PrCH\langle\begin{matrix}O\\ O\end{matrix}\rangle C_2H_4$. (125°). S. 10.—15. *Chloral* unites energetically with glycol, and the resulting compound treated with pentachloride of phosphorus gives a compound (S. G. ^{17} 1·73) which may be $CCl_3.CHCl.O.CH_2.CH_2.O.CHCl.CCl_3$ (Henry, *B.* 7, 762). If a mixture of equivalent quantities of glycol and chloral be left to stand for some days, hard transparent crystals of $C_2HCl_3OC_2H_6O_2$ [42°], H.F. 15,400, separate (De Forcrand, *C. R.* 108, 618).—16. *Phosgene* $COCl_2$ forms  $C_2H_4\langle\begin{matrix}O\\ O\end{matrix}\rangle CO$ [39°] (236°) crystallising in prisms sol. water and alcohol, insol. ether (Nembrowsky, *J. pr.* [2] 28, 439).—17. Distillation with *oxalic acid* gives formic acid, and the diformyl derivative of glycol (c. 174°) (Lorin, *C. R.* 79, 387; *Bl.* [2] 21, 409; 22, 104).–18. *Algæ* (*Spirogyra*) are able to convert glycol into starch (Bokorny, *C. C.* 1888, 858).

Sodium derivatives.—$C_2H_4(OH)(ONa)$. Formed by dissolving sodium in glycol. White crystalline deliquescent substance. Heated with vinyl bromide in a sealed tube it yields ethylene, glycol, sodium bromide, and apparently formic acid. With methyl alcohol it crystallises as $C_2H_4(OH)(ONa)MeOH$ in brilliant spangles.—With ethyl alcohol: $C_2H_4(OH)(ONa)EtOH$.—$C_2H_4(OH)(ONa)C_4H_7OH$. With glycol it forms crystalline $C_2H_4(OH)(ONa)C_2H_4(OH)_2$ (Forcrand, *C. R.* 107, 343, 1160; 108, 240).—$C_2H_4(ONa)_2$. Formed by fusing the preceding with excess of sodium. Deliquescent mass. When distilled with ethylene bromide it yields vinyl bromide, glycol, and NaBr. With $ClCO_2Et$ in ether it forms $C_2H_4(O.CO_2Et)_2$ (c. 226°) (Wallach, *A.* 226, 82).

Mono-nitrate $C_2H_5NO_4$ *i.e.* $CH_2(OH).CH_2ONO_2$. S.G. ^{11} 1·31. From glycol bromhydrin and $AgNO_3$ (Henry, *A. Ch.* [4] 27, 243). Liquid, sol. water.

Di-nitrate $C_2H_4N_2O_6$ *i.e.* $CH_2(ONO_2).CH_2(ONO_2)$. S.G. ^{8} 1·484. From glycol (42 g.), fuming HNO_3 (100 g.), and H_2SO_4 (200 g.) at 0° (H. Champion, *Z.* 1871, 469). Explosive oil.

Nitrite-nitrate (?) $C_2H_4N_2O_5$ *i.e.* $CH_2(ONO).CH_2(ONO_2)$. S.G. 1·47. Formed by passing ethylene into a cooled mixture of HNO_3 and H_2SO_4 (Kekulé, *B.* 2, 329). Oil. Sodium-amalgam forms glycol and gives off all the N as NH_3.

Aceto-nitrate $CH_2(OAc).CH_2(NO_3)$. S.G. ^{18} 1·29. From the mono-acetin, HNO_3, and H_2SO_4 (Henry, *A. Ch.* [4] 27, 259). Oil, v. e. sol. dilute HCl.

Mono-sulphuric acid $CH_2(OH).CH_2(O.SO_3H)$. From glycol and sulphuric acid (Simpson, *A.* 112, 146). Formed also by the action of sulphuric acid on glycol chlorhydrin (Oppenheim, *B.* 3, 735). Its chloride $CH_2(OH).CH_2(O.SO_2Cl)$ is formed by treating glycol with SO_2Cl_2 (Reinhard, *J. pr.* [2] 17, 342). The free acid is unstable, being decomposed by hot water into glycol and H_2SO_4. The **potassium salt** is hygroscopic. The **barium salt** BaA'_2 is v. sol. water, almost insol. alcohol.

Disulphuric acid $CH_2(OSO_3H).CH_2(OSO_3H)$. From glycol and $ClSO_3H$ at 0° (Claesson, *J. pr.* [2] 20, 5). Thick syrup, decomposed by water, especially on warming, into glycol and H_2SO_4. Its salts are insol. alcohol.—BaA'' 2aq: hair-like needles.—K_2A'': silvery mass.

Borate $(CH_2(OH).CH_2O)_3B$. [162°]. From glycol by treatment first with gaseous, then with liquid BCl_3 (Councler, *B.* 11, 1106). Minute laminæ, nearly insol. ether. Decomposed by moist air.

Mono-acetyl derivative $C_4H_8O_3$ *i.e.* $CH_2(OH).CH_2(OAc)$. *Glycol monacetin.* Mol. w. 104. (182°). Prepared by heating ethylene bromide (1 pt.) with KOAc (1 pt.) and 85 p.c. alcohol (2 pts.) at 100° in a closed bottle for two days (Atkinson, *P. M.* [4] 16, 433; *A.* 109, 232; Erlenmeyer, *A.* 192, 246) or by boiling the same mixture with inverted condenser (Maxwell Simpson, *Pr.* 9, 725). The product is fractionally distilled. Glycolic mono-acetin may also be prepared by heating glycol (1 mol.) with Ac_2O (1 mol.) for several hours at 170° (Maxwell Simpson). Colourless liquid, heavier than water. Miscible with water and alcohol. Its aqueous solution is neutral but it is easily decomposed by potash and baryta yielding glycol. Boiling with ethylene bromide and alcohol (S.G. ·82) converts it into glycol (Demole, *A.* 177, 45). AcCl forms $C_2H_4(OAc)_2$ and $CH_2Cl.CH_2.OAc$ (Lourenço, *A.* 114, 127).

Di-acetyl derivative $C_6H_{10}O_4$ *i.e.* $CH_2(OAc).CH_2(OAc)$. *Glycol diacetin.* Mol. w. 146. (187°) (Wurtz); (190°) (Perkin). S.G. ^{0} 1·128 (W.); $\frac{20}{4}$ 1·1561 (Brühl); $\frac{15}{15}$ 1·1108; $\frac{25}{25}$ 1·1018 (P.). μ_β 1·4268. R_∞ 51·79 (B.). M.M. 6·454 at 18° (Perkin, *C. J.* 45, 505). V.D. 4·74. S. 14 at 22°. *Rate of formation*: Menschutkin, *B.* 13, 1812.

Formed by heating ethylene bromide or iodide with silver acetate (Wurtz, *C. R.* 43, 199; *A.* 100, 110; *A. Ch.* [3] 55, 400). From the mono-acetin by heating with AcCl in a sealed tube at 100° and fractionally distilling the upper layer of the resulting liquid. Obtained also by heating ethylene bromide with KOAc at 150° to 200° (Demole, *A.* 177, 49). Neutral liquid; dissolves in 7 pts. of water at 22°, and is separated by $CaCl_2$ from this solution. Miscible with alcohol and ether. Boiling dilute alcohol (S.G. ·82) decomposes it into monoacetin, HOAc, and EtOAc. Resolved by bases into acetic acid and glycol.

Di-propionyl derivative $C_2H_4(OC_3H_5O)_2$. (211° cor.). S.G. $\frac{15}{15}$ 1·0544; $\frac{25}{25}$ 1·0457. M.M. 8·318 at 21·2° (Perkin, *C. J.* 45, 505).

Mono-butyryl derivative $CH_2(OH).CH_2(OC_4H_7O)$. (220°). From glycol (1 mol.) and butyric acid (1 mol.) at 200° (Lourenço, *A. Ch.* [3] 67, 267). Oil.

Di-butyryl derivative $C_2H_4(OC_4H_7O)_2$. (240°). S.G. $\frac{0}{0}$ 1·024. Obtained by heating ethylene bromide with silver butyrate and a little free butyric acid for several days at 100°, and fractionally distilling the product (Wurtz, *A. Ch.* [3] 55, 400). Oil; sol. alcohol and ether.

Acetyl butyryl derivative $CH_2(OAc).CH_2(OC_4H_7O)$. (212°). Formed by heating glycol chloro-acetin $CH_2(OAc).CH_2Cl$ with silver butyrate at 110°; or from glycol chloro-butyrin and AgOAc at 150°; in either case the product is digested with ether, and the ethereal filtrate is distilled (Maxwell Simpson, *Pr.* 10, 115). Formed also by heating glycolic mono-acetin with butyryl chloride, or glycolic mono-butyrin with AcCl (Lourenço). Heavy oil; sol. alcohol. It is but slowly decomposed by aqueous KOH even at 100°.

Acetyl-valeryl derivative $CH_2(OAc).CH_2(OC_5H_9O)$. (230°). From glycol mono-acetin and valeric acid (Lourenço, *A.* 114, 122). Neutral oil, sol. alcohol and ether.

Mono-valeryl derivative $CH_2(OH).CH_2(OC_5H_9O)$. (240°) (Lourenço, *A. Ch.* [3] 67, 268).

Di-valeryl derivative $C_2H_4(OC_5H_9O)_2$. (255°).

Stearyl derivative $C_{38}H_{74}O_4$ *i.e.* $C_2H_4(OC_{18}H_{35}O)_2$. [76°]. From silver stearate and ethylene bromide, the product being extracted with ether (Wurtz, *A. Ch.* [3] 55, 436). Small shining scales, resembling stearin.

Di-benzoyl derivative $C_{16}H_{14}O_4$ *i.e.* $C_2H_4(OBz)_2$. [67°]. (above 360°). Formed by heating silver benzoate (68 g.) with ethylene bromide (29 g.) for several days at 100°, extracting the product with ether, treating extract with slaked lime and rectifying (W.). Trimetric prisms.

Succinoxyl derivative $C_6H_{10}O_5$ *i.e.* $CH_2(OH).CH_2.O.CO.CH_2.CH_2.CO_2H$ (?) [below 100°]. Formed by heating glycol (1 mol.) with succinic acid (1 mol.) at 195° for 10 hours (Lourenço, *Rép. Chim. pure*, 1860, 179; *A.* 115, 358). Small crystals; sol. water and alcohol, sl. sol. ether.

Succinyl derivative $C_6H_8O_4$ *i.e.* $C_2H_4\left<\begin{matrix}O.CO\\O.CO\end{matrix}\right>C_2H_4$. [below 90°]. (212°) (Richter, *J. pr.* [2] 20, 207). Obtained by heating the preceding to nearly 300°. Small crystals (from alcohol); insol. water and ether, m. sol. boiling alcohol.

Mono-ethyl ether $C_4H_{10}O_2$ *i.e.* $CH_2(OH).CH_2(OEt)$. (134°) at 722 mm. S.G. $\frac{13}{13}$ ·926 (Demole, *B.* 9, 745). From mono-sodium glycol $CH_2(OH).CH_2(ONa)$ and EtI (Wurtz, *A.* 108, 84).

Di-ethyl ether $C_6H_{14}O_2$ *i.e.* $C_2H_4(OEt)_2$. (123·5°). S.G. $\frac{0}{0}$ 1·799. V.D. 4·10 (calc. 4·09). From the preceding compound by successive treatment with potassium and EtI (W.). Colourless oil with ethereal odour. Isomeric with acetal.

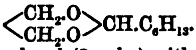
Ethyl-phenyl ether $C_2H_4(OPh)(OEt)$. (230°). S.G. $\frac{0}{0}$ 1·037 (S.); $\frac{11}{11}$ 1·018 (H.). Formed by the action of alcoholic KOEt on phenyl bromo-ethyl oxide $Ph.O.C_2H_4Br$ (Sabanéeff, *Bl.* [2] 41, 253), or on phenyl chloro-ethyl oxide (Henry. *C. R.* 96, 1233).

Ethylidene ether $C_4H_8O_2$ *i.e.* $\left<\begin{matrix}CH_2.O\\CH_2.O\end{matrix}\right>CHMe$. (82·5°). S.G. $\frac{0}{0}$ 1·000. V.D. 3·19 (calc. 3·05). Obtained by heating aldehyde with glycol for a week at 100° (Wurtz). Liquid; dissolves in 1½ vols. water, but separated from the solution by $CaCl_2$ and by KOH. Not attacked by KOH. HNO_3 forms oxalic and glycollic acids. PCl_5 gives aldehyde and $C_2H_4Cl_2$. Bromine gives liquid $C_4H_7BrO_2$ (c. 150°), whence dilute H_2SO_4 liberates glycol bromhydrin.

Propylidene ether $C_5H_{10}O_2$ *i.e.* $\left<\begin{matrix}CH_2.O\\CH_2.O\end{matrix}\right>CHEt$. (106°). V.D. 3·46. S.G. $\frac{0}{0}$ ·98. Obtained by heating propionic aldehyde (1 mol.) with glycol (2 mols.) at 100° in a sealed tube; the yield being 75 p.c. (Lochert, *A. Ch.* [6] 16, 30). Colourless limpid liquid; smelling like propionic aldehyde. Dissolves in 5 vols. water; miscible with alcohol and ether. KOH and $CaCl_2$ separate it from its aqueous solution. Completely saponified by heating with water at 130°, or by treatment with conc. HClAq. Does not reduce ammoniacal $AgNO_3$. Bromine gives a liquid bromo- derivative.

Isobutylidene ether $C_6H_{12}O_2$ *i.e.* $\left<\begin{matrix}CH_2.O\\CH_2.O\end{matrix}\right>CHPr$. (125°). V.D. 4·13 (calc. 4·02). S.G. $\frac{0}{0}$ ·964. Obtained by heating isobutyric aldehyde (1 mol.) with glycol (2 mols.) at 100°; the yield being 70 p.c. (L.). Liquid; dissolves in 6 times its volume of water, miscible with alcohol and ether. Saponified by water at 130°, by conc. HClAq, and by dilute H_2SO_4. Does not reduce ammoniacal $AgNO_3$. Bromine gives a bromo- derivative $C_6H_{11}BrO_2$ (c. 190°), insol. water, sol. alcohol and ether.

Isoamylidene ether $C_7H_{14}O_2$ *i.e.* $\left<\begin{matrix}CH_2.O\\CH_2.O\end{matrix}\right>CH.CH_2Pr$. (145°). S.G. $\frac{0}{0}$ ·944. Prepared like the preceding, using isovaleric aldehyde (L.). Liquid, v. sl. sol. water, v. sol. alcohol and ether. Saponified by water at 130°. Does not reduce ammoniacal $AgNO_3$. Bromine gives a bromo- derivative $C_7H_{13}BrO_2$ (94° at 10 mm.) which is insol. water, sol. alcohol and ether, and when saponified by dilute H_2SO_4 gives bromo- valeric aldehyde. Alcoholic KOH attacks the bromo-derivative, removing HBr and forming $\left<\begin{matrix}CH_2.O\\CH_2.O\end{matrix}\right>CH.CH{:}CMe_2$ and a small quantity of $\left<\begin{matrix}CH_2.O\\CH_2.O\end{matrix}\right>CH.CH(OH).CHMe_2$.



Heptylidene ether $\left\langle\begin{matrix}CH_2.O\\CH_2.O\end{matrix}\right\rangle CH.C_6H_{13}$. (180°). Formed by heating glycol (3 vols.) with œnanthol (1 vol.) at 130°; or from glycol (2 vols.), œnanthol (1 vol.), and a trace of HOAc at 180°; the yield being 66 p.c. (Lochert, *Bl.* [2] 48, 337; *A. Ch.* [6] 16, 35). Limpid liquid, smelling like œnanthol; v. sl. sol. water. v. sol. alcohol and ether. Completely saponified by water at 130°, or by conc. HClAq. Gaseous HCl does not act on it in the cold, but at 100° it forms glycol chlorhydrin and œnanthol, and its polymerides. PCl_5 gives ethylene chloride and œnanthol. Bromine gives a liquid mono-bromo- derivative.

Glycol chlorhydrin $C_2H_5ClO_2$ *i.e.* $CH_2(OH).CH_2Cl$. (130°). Is described as Chloro-ethyl alcohol on p. 61.

Glycol chloro-acetin *v. Acetyl derivative* of Chloro-ethyl alcohol, p. 61.

Glycol bromhydrin $C_2H_5BrO_2$ *i.e.* $CH_2(OH).CH_2Br$. *Bromo-ethyl alcohol.* (147°) (H.); (155°) (L.). S.G. $^{\underline{8}}$ 1·66 (H.). Formed, together with di-ethylenic glycol, by heating glycol (1 pt.) with ethylene bromide (1 pt.) at 120° in a sealed flask (Lourenço, *Bl.* 1, 77). Formed also by treating glycol with HBr at 100° (Henry, *A. Ch.* [4] 27, 250), and from glycol (3 mols.) and PBr_3 (1 mol.) (Demole, *B.* 9, 48). Liquid.

Nitrate $CH_2(ONO_2).CH_2Br$. (165°). S.G. $^{\underline{8}}$ 1·735. From the bromhydrin, HNO_3, and H_2SO_4 (Henry, *A. Ch.* [4] 27, 258).

Acetyl derivative $CH_2(OAc).CH_2Br$. *Glycol bromo-acetin* (162°). From glycol mono-acetin and HBr at 100° (Demole, *A.* 173, 121). Liquid, sl. sol. water. Conc. NaOHAq decomposes it, liberating ethylene oxide.

Bromo-acetyl derivative $CH_2Br.CO.O.CH_2.CH_2Br$. (230°-240°). From glycol chlorhydrin and bromine, the other products being ethylene chloro-bromide, bromo-, and di-bromo-acetic acids, and ethylene bromide (Demole, *B.* 9, 557). Slightly decomposed on distillation.

Glycol iodhydrin C_2H_5IO *i.e.* $CH_2(OH).CH_2I$. *Iodo-ethyl alcohol.* Obtained in impure condition from glycol and HI in the cold; but if the temperature is allowed to rise only ethylene iodide results (Maxwell Simpson, *Pr.* 10, 119). More easily prepared by heating the chlorhydrin with excess of powdered KI at 100° for 24 hours (Butlerow a. Ossokin, *A.* 144, 42; 145, 257). Non-volatile liquid, m. sol. water, separated from its aqueous solution by K_2CO_3. $ZnMe_2$ followed by water gives isopropyl alcohol. $ZnEt_2$ followed by water gives sec-butyl alcohol.

Acetyl derivative $CH_2(OAc).CH_2I$. *Glycolic iodo-acetin.* From glycol mono-acetin and HI; or from glycol, HOAc, and HI (Maxwell Simpson, *A.* 113, 123; *Pr.* 10, 115). Oil, which crystallises in tables at a low temperature. KOH gives ethylene oxide.

Glycol cyanhydrin $C_2H_4(OH)CN$. *Hydracrylonitrile.* (c. 220°). S.G. $^{\underline{0}}$ 1·0588. S. (ether) 2·3 at 15°. From ethylene oxide and HCy (Erlenmeyer, *A.* 191, 273). Miscible with water and with alcohol, insol. CS_2. HCl (S.G. 1·10) or aqueous NaOH give, on boiling, hydracrylic and acrylic acids.

Di-ethylenic glycol $C_4H_{10}O_3$ *i.e.* $HO.C_2H_4.O.C_2H_4.OH$. (245°-250°). S.G. $^{\underline{0}}$ 1·132. V.D. 3·78 (calc. 3·67). When an excess of ethylene oxide is heated with water in sealed tubes there is formed glycol, di-ethylenic glycol, and a small quantity of tri-ethylenic glycol (Wurtz, *A. Ch.* [3] 69, 330). By heating oxide of ethylene (1 pt.) with glycol (1 pt.) there are formed di- and tri- ethylenic glycols. By heating glycol with ethylene bromide at 115° in sealed tubes glycol bromhydrin, diethylenic glycol, other polyethylenic glycols, and water are produced; if the temperature of the mixture is allowed to rise above 130° the liquid turns brown and yields the bromhydrins of the various polyethylenic glycols (Lourenço, *C. R.* 51, 365). By using glycolic chlorhydrin instead of the bromhydrin the polyethylenic chlorhydrins may be obtained. Diethylenic glycol may also be obtained from its diacetate by treatment with an alkali. Obtained also by treating glycol mono-acetin with sodium-glycol (Mohs, *Z.* 1866, 495). Sweetish syrup; sol. water, alcohol, and ether. Nitric acid (S.G. 1·42) oxidises it to 'diglycollic acid' $CO_2H.CH_2.O.CH_2.CO_2H$, glycollic acid, and oxalic acid. Conc. HIAq gives ethylene iodide.

Mono-formyl derivative $CH_2(OH).CH_2.O.CH_2.CH_2(OCHO)$. (c. 220°). From the chlorhydrin and nitro-methane by heating for 10 hours at 200° (Pfungst, *J. pr.* [2] 34, 37).

Di-acetyl derivative $CH_2(OAc).CH_2.O.CH_2.CH_2(OAc)$. (245°-251°). Formed, together with $C_2H_4(OAc)_2$ and the di-acetyl derivatives of other polyethylenic glycols, by heating ethylene oxide with glacial HOAc or with Ac_2O at 100°, and fractionally distilling the product. Formed also from glycol diacetin and ethylene oxide (Wurtz, *C. R.* 50, 1195; *A.* 116, 249).

Chlorhydrin $C_4H_9ClO_2$ *i.e.* $CH_2(OH).CH_2.O.CH_2.CH_2Cl$. (180°-185°). From ethylene oxide and glycolic chlorhydrin at 140° (Wurtz, *A. Ch.* [3] 69, 338). Also from ethylene oxide and gaseous HCl; and from glycol and glycol chlorhydrin at 140° (Lourenço, *A. Ch.* [3] 67, 290).

Bromhydrin $C_4H_9BrO_2$ *i.e.* $HO.C_2H_4.O.C_2H_4Br$. (205°). From glycol and $C_2H_4Br_2$ at 160° (L.).

Tri-ethylenic glycol $C_6H_{14}O_4$ *i.e.* $CH_2(OH).CH_2.O.CH_2.CH_2.O.CH_2.CH_2(OH)$. (c. 290°). S.G. 1·138. Formed by heating glycol with ethylene oxide (*v. supra*). Thick liquid, miscible with water and alcohol, sl. sol. ether. Oxidised by nitric acid to 'diglycolethylenic' acid $(CO_2H.CH_2.O)_2C_2H_4$; a syrupy acid which crystallises with difficulty and forms crystalline salts: KHA''.—CaA'' 3aq.—Ag_2A''.

Di-acetyl derivative $O_2(C_2H_4)_3(OAc)_2$. (290°-300°). From ethylene oxide (2 mols.) and glycol diacetin. Liquid, miscible with water, alcohol, and ether.

Chlorhydrin $C_6H_{13}ClO_3$. (222°-232°). From ethylene oxide (2 mols.) and glycolic chlorhydrin (1 mol.). Liquid, sol. water.

Bromhydrin $C_6H_{13}BrO_3$. (250°). Slightly decomposed on distillation.

Tetra-ethylenic glycol $C_8H_{18}O_5$ *i.e.* $(CH_2(OH).CH_2.O.C_2H_4)_2O$. (300°); (230° at 25 mm.). Formed as above from glycol and ethylene bromide.

Diacetyl derivative $C_8H_{16}Ac_2O_5$. (above 320°). From ethylene oxide (3 mols.) and glycol diacetin (1 mol.).

Chlorhydrin $C_8H_{17}ClO_4$. (262°–272°). Liquid, sol. water.

Penta-ethylenic glycol $C_{10}H_{22}O_6$ *i.e.* $(CH_2(OH).CH_2.O.C_2H_4.O)_2C_2H_4$. (281° at 25 mm.). Liquid, sol. water, alcohol, and ether.

Hexa-ethylenic glycol $C_{12}H_{26}O_7$ *i.e.* $(CH_2(OH).CH_2.O.C_2H_4.O.C_2H_4)_2O$. (325° at 25 mm.). Viscid liquid (L.).

GLYCOLAMIC ACID *v.* GLYCOLLAMIC ACID.

DI-GLYCOL-ETHYLENIC ACID *v. Tri-ethylenic* GLYCOL.

GLYCOLIGNOSE *v.* CELLULOSE.

GLYCOLINE $C_6H_{10}N_2$. (155°). S.G. ^{12} 1·008. A base formed by distilling glycerin (6 pts.) with ammonium chloride in a current of NH_3 (Etard, *C. R.* 92, 460, 795). Liquid, smelling like pyridine. Miscible with water, alcohol, and ether. With EtI it forms a compound $C_6H_{10}N_2EtI$ crystallising in lemon-yellow needles.—$C_6H_{10}N_2HCl$: needles, v. e. sol. water and alcohol.

GLYCOLLAMIC ACID $NH_2.CH_2.CO_2H$ *v.* GLYCOCOLL.

Diglycollamic acid $C_4H_7NO_4$ *i.e.* $NH(CH_2.CO_2H)_2$. *Imido-di-acetic acid.* S. 2·43 at 5°. When chloro-acetic acid is boiled with conc. NH_3Aq for 12 hours there is formed a mixture of glycocoll, diglycollamic acid, triglycollamic acid, and a little glycollic acid. The solution, after being freed from most of the NH_4Cl by ppn. with alcohol is boiled with $Pb(OH)_2$. The pp. thus obtained contains lead triglycollamate (whence the acid may be liberated by H_2S), and the solution, freed from lead by H_2S, is boiled with ppd. $ZnCO_3$, when insoluble zinc diglycollamate is formed, zinc glycocoll remaining in solution (Heintz, *A.* 122, 257; 124, 297; 136, 213; 145, 49; 156, 54). Trimetric prisms, insol. alcohol and ether; m. sol. water, forming an acid solution. Forms a nitrosamine with nitrous acid.

Salts.—NH_4HA'': prisms, v. e. sol. water, insol. alcohol.—$BaH_2A''_2$: amorphous, v. sol. water.—$CuA''2aq$: small blue prisms, sl. sol. boiling water.—PbA'': slender needles.—ZnA'': minute tables, nearly insol. water.—Ag_2A'': crystalline pp., insol. water.—$Ag_2A''HNO_3 4aq$: prisms, insol. alcohol.—$H_2A''HCl$: tables, v. e. sol. water, m. sol. alcohol.—$H_2A''HNO_3$. —$(H_2A'')_2H_2SO_4$: small prisms. Decomposed by water into H_2SO_4 and H_2A''.—$H_2A''H_2SO_4$: formed by boiling the preceding with alcohol.

Amide $C_4H_9N_3O_2$ *i.e.* $NH(CH_2.CO.NH_2)_2$. Prepared, together with the amide of triglycollamic acid, by heating chloro-acetic ether with ammonia at 60° to 70°, evaporating, washing with ether, dissolving in water, and ppg. the mixed hydrochlorides with alcohol. The amides are liberated by Ag_2O, and may be separated by alcohol, which dissolves only the amide of diglycollamic acid (Heintz, *Z.* [2] 5, 161). Trimetric tables (from water); m. sol. water, sl. sol. hot, nearly insol. cold, alcohol. Its aqueous solution is alkaline.—$B'HCl$: prisms (from water), sl. sol. alcohol.—$B'_2H_2PtCl_6$: six-sided tables (from water), insol. alcohol.—$B'HAuCl_4$: thin six-sided tables (from water) or long needles (from alcohol).

Anilide $NH(CH_2.CO.NHPh)_2$. [141°]. Formed by digesting the chloro-acetyl derivative of aniline with alcoholic ammonia at 100°, evaporating, and crystallising from water (P. J. Meyer, *B.* 8, 1154). Needles; m. sol. hot water, v. sol. ether and alcohol, sl. sol. cold water. When boiled with aqueous NaOH it gives off aniline. Its nitrate crystallises in needles [172°]. Tommasi (*Bl.* [2] 22, 3) by the action of alcoholic NH_3 on the chloro-acetyl derivative of aniline at 50° obtained an amorphous compound $C_8H_{11}NO_3$

p-Toluide $NH(CH_2.CO.NHC_7H_7)_2$. [150°]. From the chloro-acetyl derivative of toluidine and alcoholic NH_3 at 100° (Meyer, *B.* 8, 1155). Rosettes of long silky needles (from dilute alcohol); sl. sol. boiling water, m. sol. cold alcohol, v. sol. ether.

Ureïde $NH(CH_2.CO.NH.CO.NH_2)_2$. [195°–200°]. From bromo-acetyl-urea and dry or alcoholic NH_3 at 80°–100° (Mulder, *B.* 5, 1011). Slender needles; sl. sol. cold, m. sol. warm, water. V. sol. dilute HClAq and reppd. by NH_3. —$B'HCl$: crystals. — $B'_2H_2PtCl_6$: needles or prisms.

Nitrosamine $NO.N(CH_2.CO_2H)_2$. [above 100°]. Small pale yellow tables, m. sol. water, alcohol, and ether.—$CaA''aq$: more sol. cold than hot water, nearly insol. alcohol.—$BaA''\frac{1}{2}aq$: crystalline crusts.—Ag_2A'': sparingly soluble prisms (Heintz, *A.* 138, 301).

Triglycollamic acid $C_6H_9NO_6$ *i.e.* $N(CH_2.CO_2H)_3$. S. ·134 at 5°. Formed by boiling chloro-acetic acid with NH_3 (*v. supra*), or diglycollamic acid with chloro acetic acid (Heintz, *A.* 122, 239; 136, 221; Lüddecke, *A.* 147, 272; Ziegler, *Z.* [2] 5, 659). Small prisms. Does not combine with acids. Fuming HCl at 200° splits it up into diglycollamic and glycollic acids. Nitrous gas does not act on it. Zinc and dilute H_2SO_4 reduce it to ethyl-diglycollamic acid.

Salts.—$(NH_4)_2HA'''aq$: needles.—$K_2HA'''aq$: needles, v. sol. water.—$BaHA'''aq$: prisms, sl. sol. water.—$Ba_3A'''_2 4aq$: laminæ, insol. water.—$PbHA''2aq$: prisms. S. 3·3.—$Pb_3A'''_2$: laminæ. —Ag_3A''': crystalline pp.

Ethyl ether Et_3A'''. (280°–290°). From the silver salt and EtI (Heintz, *A.* 140, 264). Liquid, more sol. cold than hot water.

Amide $N(CH_2.CO.NH_2)_3$. From the preceding ether and NH_3. Also from chloro-acetic ether and NH_3. Rectangular tables (from alcohol); v. sol. hot water, sl. sol. alcohol. Neutral to litmus.—$B'HCl$: trimetric prisms (from water). —$B'_2H_2PtCl_6$: tables or laminæ, insol. alcohol and ether.—$B'HAuCl_4$.

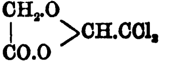
GLYCOLLIC ACID $C_2H_4O_3$ *i.e.* $HO.CH_2.CO_2H$. *Oxyacetic acid.* Mol. w. 76. [79°].

Occurrence.—In the grease of sheep's wool as the potassium salt; separated therefrom by forming the lead salt, decomposing this with H_2SO_4, and extracting with ether (Buisine, *C. R.* 107, 789). Occurs also in the juice of unripe grapes and in the leaves of the wild vine (*Ampelopsis hederacea*) (Erlenmeyer, *Z.* 1866, 639; Gorup-Besanez, *A.* 161, 229).

Formation.—1. From hippuric acid either by treatment with nitrous acid and decomposition of the resulting benzoyl-glycollic acid by boiling dilute H_2SO_4, or by treatment with dilute H_2SO_4 and decomposition of the resulting glycocoll by nitrous acid (Socoloff a. Strecker, *A.* 80, 18).—2. Tartronic acid $CO_2H.CH(OH).CO_2H$ is heated to 180°; the residue, consisting of nearly pure glycollide, is dissolved in aqueous KOH, silver nitrate is then added, and the ppd. silver glycollate decomposed by HCl (Dessaignes, *C.R.* 38, 44). 3. From glyoxal by the action of alkalis (Debus) and even of water. Thus, when glyoxal is heated with water at 150°, one-third of it is converted into glycollic acid (De Forcrand, *C. R.* 98, 295).—4. By boiling silver bromo-acetate with water. By boiling iodo-acetic acid with moist Ag_2O, or lead iodo-acetate with water (Perkin a. Duppa, *P. M.* [4] 18, 54). In like manner by boiling chloro-acetic acid with caustic alkalis or by heating crystallised chloro-acetate of potassium or sodium (Kekulé, *A.* 105, 286). By boiling chloro-acetonitrile with lime-water (Beckurts a. Otto, *B.* 9, 1591).—5. By allowing a solution of glycol (1 vol.) in nitric acid (4 vols. of S.G. 1·33) to stand for some days (Wurtz, *C. R.* 44, 1306).—6. Together with other products from propylene glycol by oxidation with HNO_3, or with air and platinum black (Wurtz, *C. R.* 45, 306).—7. By placing in a tall cylinder layers of alcohol, water, and conc. nitric acid one above another, and leaving the liquids to mix by diffusion, which they do in about a week (Debus, *A.* 100, 1). Glyoxal, glyoxylic acid, oxalic acid, aldehyde, and acetic acid are formed at the same time.—8. Found in the mother-liquor in the preparation of mercuric fulminate (Cloez, *C. R.* 34, 364; Fahlberg, *J. pr.* [2] 7, 331).—9. By the action of zinc and dilute H_2SO_4 on oxalic acid (Schulze, *Z.* 1862, 616, 682; Church, *C.J.* 16, 301).—10. By boiling an aqueous solution of oxalic acid for eight days with zinc (Crommydis, *Bl.* [2] 27, 3; De Forcrand, *Bl.* [2] 39, 310).—11. By the action of nitric acid on acrolein (Claus, *A. Suppl.* 2, 119). 12. When tartaric acid is warmed with conc. H_2SO_4 at 45° it gives off CO, CO_2, and SO_2, and the residue contains glycollic and pyruvic acids as well as tartaric and racemic acids. The acids are separated by crystallisation, first of their barium, and then of their calcium, salts (Bouchardat, *C. R.* 89, 99).—13. From acetylene tetrachloride and alcoholic KOH at 100° (Berthelot, *Z.* 1869, 683).—14. From di-chloro-vinyl ethyl oxide and water at 130° (Geuther a. Brockhoff, *J. pr.* [2] 7, 114).—15. Occurs among the products of the action of HNO_3 on glycerin.—16. Together with gluconic and formic acids, by the action of red HgO and baryta-water on glycerin (Herzfeld, *A.* 245, 27). Also from glycerin and Ag_2O (Kiliani, *B.* 16, 2415).—17. By heating cupric acetate (2 pts.) with water (5 pts.) at 200°, cuprous oxide being ppd. (Cazeneuve, *C. R.* 89, 525).—18. By oxidising inulin with HNO_3 (Kiliani, *A.* 205, 168).—18. From glucose or lævulose by oxidation with Ag_2O.

Preparation.—1. A solution of 10 grms. of commercial glycerin (85 p.c.) and 6 grms. of $Ca(OH)_2$ in 200 c.c. of water is heated on a water-bath with precipitated Ag_2O (prepared from 60 grms. of $AgNO_3$) for four hours. The liquid is then filtered, saturated with CO_2, boiled, again filtered, and evaporated till the calcium glycollate crystallises out; the yield is 4·6 grms. (Kiliani, *B.* 16, 2414).—2. Crude sugar (1 pt.) is heated with 2 p.c. sulphuric acid (20 pts.), the sulphuric acid removed by barium carbonate, and to the filtrate are added calcium carbonate (2 pts.) and silver oxide (10 pts.). The mixture is heated to 80° until gas ceases to be evolved; it is then filtered and evaporated, when calcium glycollate separates out (Kiliani, *A.* 205, 191).—3. A few grammes of strong alcohol are gently heated in a capacious vessel, with a small quantity of nitric acid, till the vessel becomes filled with red fumes of nitrous acid; and when the action has been thus set up, about 500 grms. dilute alcohol of 20 per cent., and 440 grms. nitric acid of specific gravity 1·34 are poured in. The reaction, which must be moderated by immersing the vessel in water at 20°C., is complete in about 12 hours. The liquid is evaporated in small portions over a water-bath, neutralised with lime and the mixture of glycollate of calcium, glyoxal, and glyoxylate of calcium boiled for several hours with milk of lime, whereby both the glyoxal and the glyoxylic acid are converted into glycollic acid. The hot filtrate freed from excess of lime by carbonic acid yields tolerably pure glycollate of calcium; and by decomposing this salt with oxalic acid, neutralising the filtrate with carbonate of lead, and evaporating, the neutral glycollate of lead is obtained in well-developed crystals. The hot aqueous solution of this salt, decomposed by an equivalent quantity of dilute sulphuric acid, yields a solution of glycollic acid, which may be crystallised by evaporation to a syrup at 60° or 70°C., afterwards *in vacuo* over oil of vitriol, and purified by recrystallisation from anhydrous ether (Lautemann, *Kolbe's Org. Chem.*; Drechsel, *A.* 127, 150).—4. By boiling chloro-acetic acid with water or with water and calcium carbonate (Fittig, *B.* 9, 1198; Thomson, *A.* 200, 76; Hölzer, *B.* 16, 2955).

Properties.—Needles (from water) or plates (from ether). When not quite pure it is deliquescent. V. sol. alcohol and ether. Scarcely extracted by ether from its aqueous solution. Very slightly volatile with steam. When strongly heated it gives off pungent fumes and forms glycollide and formic paraldehyde (Krupsky, *Z.* [2] 5, 177). Conc. HNO_3 oxidises it to oxalic acid. According to Claus (*A.* 145, 256) it may be reduced to acetic acid by zinc and H_2SO_4. Conc. HBrAq at 100° slowly converts it into bromo-acetic acid (Kekulé, *A.* 130, 11). Glycollic acid yields methane (2 vols.) and hydrogen (1 vol.) when distilled with excess of quicklime (Hanriot, *Bl.* [2] 45, 80; *C. R.* 101, 1156). With chloralide at 125° it slowly forms



$\begin{array}{l} CH_2.O \\ | \\ CO.O \end{array} \!\!>\! CH.CCl_3$ [41°], which forms small crystals, sol. alcohol, ether, and chloroform (Wallach, *A.* 193, 35).

Salts.—$NH_4HA'_2$: slender needles; v. sol. water and hot alcohol.—NaA'aq: small crystals (from water).—NaA' ½aq (from dilute alcohol).—$NaHA'_2$: silky needles.—$Na_2C_2H_2O_3$2aq: small deliquescent needles (De Forcrand, *Bl.* [2] 40, 104).—TlA': long pointed needles.—KA'½aq: silky needles.—$CaA'_2$8aq (Lubavin, *J. R.* 14, 287).—$CaA'_2$5aq.—$CaA'_2$4aq (Fittig, *J. pr.* [2] 10, 271).—$CaA'_2$3aq (Debus; Böttinger, *A.* 198, 228).—$CaA'_2$1½aq: stellate groups of asbestos-like needles; sl. sol. cold water.—CaA'_2. Obtained by evaporating a solution at 100° (Fahlberg; Carius, *J. pr.* [2] 9, 303). Crusts of small crystals. S. 1·2 at 10° (Debus, *A.* 166, 117); 5·3 at 100° (Fahlberg).—$CaA'_2CaCl_2$6aq: separates from a highly concentrated solution containing the two salts in large octahedra, permanent over sulphuric acid in the exsiccator (Jazukovitch, *Z.* 1864, 62).—$CaA'_2CaCl_2$2aq (Böttinger). A double calcium salt of glycollic and glyoxylic acids $CaC_4H_6O_6(CaC_4H_6O_8)_2$2aq crystallises from the product of the oxidation of alcohol.—$SrA'_2$5aq: minute slender needles, nearly insol. alcohol (Scheiber, *J. pr.* [2] 13, 436). S. 3·3 at 19°.—BaA'_2: monoclinic prisms. S. 13 at 17°.—$MgA'_2$2aq: extremely thin minute needles. S. 8 at 18° (Scheiber). V. sol. boiling water.—$ZnA'_2$2aq: tufts of needles or prisms. S. 3 at 17°. Readily forms supersaturated solutions (Schulze).—PbA'_2: monoclinic crystals resembling gypsum. S. 3 at 15°.—PbA'_2PbO: from the calcium salt and lead subacetate. Crystalline. S. ·01.—PbA'_2PbCl_2. Formed by adding lead chloride to the ammonium salt (Engel, *Bl.* [2] 44, 424).—CuA'_2: blue crystals. S. ·7 in the cold.—HgA'_2HgCl_2: prisms, sl. sol. cold water. Formed by boiling chloro-acetic acid with HgO.—AgA': spangles, sl. sol. cold water; decomposed by boiling water. Insol. alcohol (Kekulé).—AgA'aq: large crystals (Dessaignes).—AgA'$\frac{1}{2}$aq: monoclinic laminæ (Naumann, *A.* 129, 278).

Acetyl derivative $AcO.CH_2.CO_2H$. From glycollic acid and Ac_2O at 160° (Senff, *A.* 208, 277). Small prisms, v. e. sol. water, v. sl. sol. alcohol. Decomposed by alkalis into acetic and glycollic acids.—$CaA'_2$2aq: from acetyl-glycollic ether by boiling with lime (Heintz, *A.* 123, 325).

Benzoyl derivative $BzO.CH_2.CO_2H$. Formed by the action of nitrous acid on hippuric acid (Strecker, *A.* 68, 54; Strecker a. Socoloff, *A.* 80, 18). It may also be prepared by slowly passing chlorine into a solution of hippuric acid in moderately dilute KOH, neutralising with HCl, evaporating and extracting with ether (Gössman, *A.* 90, 181; Strecker, *A.* 91, 359). Prisms (from alcohol) or laminæ. Sl. sol. cold, m. sol. hot, water; v. sol. alcohol and ether. Melts under water. Gives off benzoic acid when heated strongly. Decomposed by boiling water into benzoic and glycollic acids; this hydrolysis is accelerated by the presence of mineral acids. Sodium-amalgam forms 'benzoleic' acid $C_7H_{10}O_2$ and an acid $C_{18}H_{24}O_7$, which has an odour of excrement, is insol. water and ether, but v. sol. alcohol, and forms gummy $BaC_{18}H_{22}O_7$ (Otto, *A.* 145, 350). Salts.—$NaC_9H_7O_4$3aq.—$CaA'_2$2aq.—CaA'_2aq: slender needles. S. 2·36 at 11°; 13·3 at 100°. Readily forms supersaturated solutions. Forms a double salt with $CaCl_2$.—$BaA'_2$2aq: delicate silky needles.—PbA'_2.—$(PbA'_2)_2PbO$ 3aq.—$(FeA'_3)_2(Fe_2O_3)_3$31aq: voluminous flesh-coloured pp.—$ZnA'_2$4aq.—AgA'.

m-Chloro-benzoyl derivative $C_6H_4Cl.CO.O.CH_2.CO_2H$. From *m*-chloro-hippuric acid and nitrous acid (Otto, *A.* 122, 164). Waxy crystalline mass, sl. sol. water.

Methyl ether $HO.CH_2.CO_2Me$. (151° i.V.). S.G. $\frac{0}{0}$ 1·1868 (Schreiner, *B.* 12, 179; *A.* 197, 1).

Ethyl ether $HO.CH_2.CO_2Et$. (160° i.V.). S.G. $\frac{0}{0}$ 1·1078 (Schreiner). Formed by treating chloro-acetic ether with rather more than an equivalent quantity of sodium glycollate (or of sodium acetate in presence of alcohol) at 140° (Heintz, *P.* 114, 440; *A.* 123, 326; Schreiner, *A.* 197, 5). Prepared by heating glycollide with alcohol in sealed tubes at 200° (Norton a. Tscherniak, *C. R.* 87, 30). Liquid, which dissolves in water forming a neutral solution from which it may be separated by K_2CO_3. Boiling alkalis decompose it into alcohol and glycollic acid. With aqueous NH_3 it forms the amide (*v. infra*). It combines with $CaCl_2$. With PCl_5 it reacts in the cold forming chloro-acetic ether (Henry, *B.* 3, 705); excess of PCl_5 at 150° gives chloro-acetyl chloride. A mixture of HNO_3 and H_2SO_4 forms $NO_2.O.CH_2.CO_2Et$ (181°). S.G. $\frac{15}{}$ 1·211 (Henry, *A. Ch.* [4] 28, 424). Cyanic acid forms the allophanyl derivative [144°] of which the corresponding acid melts at 192° (Traube, *C. C.* 1888, 1435).

Acetyl derivative of the ethyl ether $AcO.CH_2.CO_2Et$. (179°). S.G. $\frac{17}{}$ 1·009. Prepared by heating chloro-acetic ether with dry NaOAc at 170°. Formed also by the action of alcoholic KOAc on bromo-acetic ether (Gal, *A.* 142, 370). Formed also by passing chlorine into a cooled alkaline solution of aceturic ether (Curtius, *B.* 17, 1673). Liquid, sl. sol. water. NH_3 converts it into acetamide and the amide of glycollic acid. Solid KOH saponifies it. HBr forms ethyl bromide, HOAc, and bromo-acetic acid. HI, even in the cold, forms EtI, acetic ether, and HOAc.

Propionyl derivative of the ethyl ether $C_3H_5O.O.CH_2.CO_2Et$. (200°). S.G. $\frac{22}{}$ 1·005. From chloro-acetic ether and sodium propionate at 175° (Senff, *A.* 208, 274). Colourless, strongly refracting, liquid, v. sl. sol. cold water.

Butyryl derivative of the ethyl ether $C_4H_7O.O.CH_2.CO_2Et$. (206°). S.G. $\frac{22.5}{}$ 1·029. From bromo-acetic ether by heating with potassium butyrate (Gal, *Bl.* [2] 7, 329).

Isobutyryl derivative of the ethyl ether $Pr.CO.O.CH_2.CO_2Et$. (197°). S.G. $\frac{22}{}$ 1·024 (Senff, *A.* 208, 271).

Carbonyl derivative of the ethyl ether $C_9H_{17}O_7$ *i.e.* $CO(OCH_2.CO_2Et)_2$. *Carbo-diglycollic ether.* (280°). Formed, together with ethyl-chloro-formate and glycollide, when gaseous carbonyl chloride $COCl_2$ is passed through glycollic ether (Heintz, *A.* 154, 257). Viscid heavy oil, v. sol. alcohol and ether. Readily decomposed by bases into carbonate and glycollate.

Carboxy-glycollic ether $C_7H_{12}O_5$ *i.e.* $CO_2Et.O.CH_2.CO_2Et$. (c. 240°). Formed by heating chloro-formic ether with glycollic ether (Heintz). Heavy oil, v. e. sol. alcohol and ether.

Benzoyl derivative of the ethyl ether $C_{11}H_{12}O_4$ *i.e.* $BzO.CH_2.CO_2Et$. (287° cor.). S.G. $\frac{20}{}$ 1·1509. From chloro-acetic ether and NaOBz at 180° (Andrejeff, *A.* 133, 284). Also from diazo-acetic ether by heating with benzoic acid (Curtius). Oil.

Propyl ether $HO.CH_2.CO_2Pr$. (171° i.V.). S.G. $\frac{0}{0}$ 1·0640 (Schreiner, *A.* 197, 1).

Chloride $HO.CH_2.COCl$. From glycollic acid and PCl_5 (Fahlberg, *J. pr.* [2] 7, 343). Excess of PCl_5 at 120° gives chloro-acetyl chloride.

Amide $HO.CH_2.CONH_2$. [120°]. Formed by dissolving glycollide in aqueous ammonia (Heintz, *A.* 123, 322). Formed also by the action of aqueous NH_3 on glycollic ether. Left as a residue when ammonium tartronate is heated above 150° (Dessaignes, *C. R.* 38, 47). Crystals (from water). V. sol. water, m. sol. alcohol (its isomeride glycocoll is nearly insol. alcohol). Does form salts with bases. Does not hinder the ppn. of $Cu(OH)_2$. Boiling KOHAq converts it into glycollic acid. Dilute HClAq does the same.

Ethylamide $HO.CH_2.CO.NHEt$. (250°). From chloro-acetic ether and alcoholic ethylamine (Heintz, *A.* 129, 27). Syrup; miscible with water and alcohol, sol. ether. Decomposed by alkalis, even in the cold, into ethylamine and glycollic acid.

Anilide $HO.CH_2.CO.NHPh$. [108°]. S. 6 at 20°; 100 at 100°. From glycollide and aniline at 130° (Norton a. Tscherniak, *C. R.* 86, 1332). Monoclinic needles; v. e. sol. alcohol and ether.

Di-bromo-o-toluide $HO.CH_2.CO.NH.C_6H_2Br_2Me$. [182°]. From its acetyl derivative $AcO.CH_2.CO.NH.C_6H_2Br_2Me$ [172°], which is got by heating the compound $Br.CH_2.CO.NH.C_6H_2Br_2Me$ with acetamide at 160° (Abenius a. Widmann, *J. pr.* [2] 38, 285). Needles (from alcohol).

Acetyl derivative of the nitrile $C_4H_5NO_2$ *i.e.* $AcO.CH_2CN$. (175°). S.G. $\frac{13\cdot5}{}$ 1·100. From chloro-acetonitrile and alcoholic KOAc (Henry, *C. R.* 102, 768). Liquid, smelling like acetic acid. Has a sweetish bitter taste. M. sol. water. With HCl it yields chloro-acetic acid (?).

Anhydride v. GLYCOLLIDE.

Methyl derivative $MeO.CH_2.CO_2H$. (178°). S.G. 1·180. Prepared by dissolving sodium (2 atoms) in methyl alcohol and mixing the solution with chloro-acetic acid (1 mol.). Purified by means of its zinc-salt. Thick syrup, miscible with water. Not decomposed by boiling alcoholic NaOH. Salts.—KA′4aq: large prisms (from water); permanent in the air. Readily forms super-saturated solutions. Sol. alcohol.—NaA′: deliquescent.—$CaA'_2$2aq: gummy, but becomes crystalline over H_2SO_4.—BaA'_2: prisms, v. sol. water, nearly insol. alcohol.—PbA'_2: crystalline mass, sol. water and alcohol.—$CuA'_2$2aq: greenish monoclinic prisms, sol. water and alcohol.—ZnA'_2 2aq: acute trimetric octahedra. S. 27·4 at 18·4°. Sol. alcohol.—AgA′: delicate flat needles (from hot water).

Methyl derivative of the methyl ether $MeO.CH_2.CO_2Me$. (133°) (Schreiner, *B.* 12, 179); (127° i.V.) (Fölsing, *B.* 17, 486). S.G. $\frac{0}{0}$ 1·0890 (S.). Volatile with steam.

Methyl derivative of the ethyl ether $MeO.CH_2.CO_2Et$. (139°) (S.); (131°) (F.). S.G. $\frac{0}{0}$ 1·0740.

Methyl derivative of the propyl ether $MeO.CH_2.CO_2Pr$. (147° i.V.). S.G. $\frac{0}{0}$ 1·0552.

Ethyl derivative $EtO.CH_2.CO_2H$. *Ethyl-glycollic acid.* (199°) (Schreiner). Formed by the action of alcoholic NaOEt on chloro-acetic acid (Heintz, *P.* 109, 489; 111, 552). The resulting mixture is filtered from NaCl, evaporated, dissolved in water, and mixed with cupric sulphate in quantity rather more than equivalent to the sodium used. The mixture is evaporated over the water-bath, and the residue is exhausted with alcohol which extracts cupric ethyl-glycollate. After purification by crystallisation this salt is decomposed by H_2S. Ethyl-glycollic acid is also formed from $CH_2Cl.CCl_3$ and excess of NaOEt (Geuther a. Brockhoff, *J. pr.* [2] 7, 101). Liquid. Partially decomposed on distillation with production of formic paraldehyde. When boiled for a long time with inverted condenser it forms glycollic acid and ethyl-glycollic ether. HIAq gives EtI and glycollic acid. Salts.—BaA'_2: crystallises with difficulty; v. sol. water and alcohol.—$CaA'_2$2aq: minute needles (from alcohol-ether).—$CuA'_2$2aq: blue prisms. S. 14·2 at 14°.

Ethyl-derivative of the methyl ether $EtO.CH_2.CO_2Me$. (142° i.V.); (148°) (F.). S.G. $\frac{0}{0}$ 1·0145 (Schreiner, *A.* 197, 1).

Ethyl derivative of the ethyl ether $EtO.CH_2.CO_2Et$. *Ethyl-glycollic ether.* (158°) (S.); (152°) (F.). S.G. $\frac{0}{0}$ ·9996. Obtained as above; also from chloro-acetic ether and NaOEt (Henry, *B.* 4, 706). Formed also by treating $EtO.CH_2.CO_2Na$ with alcohol and EtI.

Ethyl derivative of the propyl ether $EtO.CH_2.CO_2Pr$. (166° i.V.). S.G. $\frac{0}{0}$ ·9944.

Ethyl derivative of the isoamyl ether $EtO.CH_2.CO_2C_5H_{11}$. (180°–190°). From sodium ethyl-glycollate and isoamyl iodide in alcohol (O. Siemens, *J.* 1861, 452).

Ethyl derivative of the chloride $EtO.CH_2.COCl$. (128°). S.G. ^{1} 1·145. From the acid and PCl_5 (Henry, *B.* 2, 276).

Ethyl derivative of the amide $EtO.CH_2.CONH_2$. (225°). From $EtO.CH_2.CO_2Et$ and cold NH_3Aq. Trimetric prisms. Melts below 100°. V. e. sol. water, v. sol. alcohol and ether. Gives with Br and KOHAq the urea $EtO.CH_2.NH.CO.NH.CO.CH_2.OEt$ [80°] (Hofmann, *B.* 18, 2734).

Ethyl derivative of the nitrile $EtO.CH_2.CN$. (133°). S.G. ^{20} ·909. Formed by distilling the amide $EtO.CH_2.CONH_2$ (40 g.) with P_2O_5 (60 g.) (Norton a. Tscherniak, *C. R.* 87, 27). Liquid, sl. sol. water, v. sol. alcohol and ether.

Tri-chloro-ethyl derivative $CCl_3.CH_2.O.CH_2.CO_2H$. [70°]. Formed, together with chloro-acetic acid, by warming tri-chloro-ethyl alcohol with aqueous KOH (Garzarolli-Thurnlackh, *A.* 210, 71). Small plates (from water). V. sol. alcohol, ether, and boiling water.—$CaA'_2$3aq: needles, m. sol. water.—AgA′: needles.

Propyl derivative of the methyl ether $PrO.CH_2.CO_2Me$. (179° i.V.). S.G. $\frac{0}{0}$ ·9850 (Schreiner).

Propyl derivative of the ethyl ether $PrO.CH_2.CO_2Et$. (185° i.V.). S.G. $\frac{0}{0}$ ·9760.

Propyl derivative of the propyl ether $PrO.CH_2.CO_2Pr$. (192° i.V.). S.G. $\frac{0}{0}$ ·9778.

Isoamyl derivative $C_5H_{11}O.CH_2.CO_2H$. (235°). S.G. 1·003. From sodium isoamylate, isoamyl alcohol, and chloro-acetic acid (Heintz, *P.* 109, 301). Liquid, sl. sol. water, miscible with alcohol and ether.—NaA′2aq: [190°–200°]; thin rectangular plates (from alcohol); v. sol. water and alcohol, insol. ether.—KA′aq: [200°–210°]; long prisms or thin plates. Pp. by adding ether to its alcoholic solution.—$Hg_2A'_2$: [170°]; white powder, v. sl. sol. water, sl. sol. alcohol.—CuA'_2: minute bluish-green prisms; v. sl. sol. water, m. sol. alcohol.—AgA′: slender needles (from water).

Isoamyl derivative of the ethyl ether $C_5H_{11}O.CH_2.CO_2Et$. (212°). From sodium isoamyl-glycollate $C_5H_{11}O.CH_2.CO_2Na$ and EtI in alcoholic solution at 100° (Siemens).

Phenyl derivative $C_8H_8O_3$ *i,e.* $C_6H_5O.CH_2.CO_2H$. *Phenoxy-acetic acid.* [97°]. (285°). S. 1. *Formation.*—1. By heating NaOPh with chloro-acetic acid (Heintz, *J.* 1859, 361).—2. By heating tri-bromo-ethylene with alcohol, KOH, and phenol at 170° (Sabanejeff a. Dworkowitsch, *A.* 216, 284). *Preparation.*—1. Equivalents of phenol (1 part) and chloro-acetic acid are melted together and (300 pts. of) solution of NaOH (S.G. 1·3) is added. The resulting crystalline mass is pressed out, dissolved in water and acidified with HCl. The acid separates as an oil which soon becomes crystalline (Giacosa, *J.pr.* [2] 19, 396).—2. By stirring in an iron pan a concentrated solution of sodic chloro-acetate (12 pts.) with sodic phenylate (10 pts.). As soon as the first reaction is over, the mass is heated, with constant stirring until it becomes pasty. This is dissolved in water before it is quite cold. The acid is thrown down by HCl and crystallised from water (Fritzsche, *J.pr.* [2] 20, 269). The yield is 90 per cent. *Properties.*—White needles (from water). Taste both acid and bitter. Antiseptic. Scarcely volatile with steam. Soluble in ether, glacial acetic acid, benzene and CS_2. Etherified on keeping in alcoholic solution for 24 hours. *Reactions.*—1. $FeCl_3$ gives a yellow pp.—2. Dilute *nitric acid* (S.G. 1·19) converts it into di-nitro-phenol.—3. *Bromine-water* forms $C_6H_4Br.O.CH_2.CO_2H$ (Giacosa).—4. Violently attacked by PCl_5 forming $PhO.CCl_2.CCl_2$ and $C_6H_4Cl.O.CH_2.COCl$ (Michael, *J. pr.* [2] 35, 96). Salts.—NaA′½aq. Needles (from alcohol).—KA′. Scales (F.). Needles (G.).—NH_4A'. Scales (F.).—CaA′ 3½aq.—BaA'_2 3aq.—CuA'_2 2aq : sparingly soluble minute prisms.—AgA′: slender needles grouped concentrically. Methyl ether.—MeA′. (245° uncor.). S.G. $\underline{17\cdot5}$ 1·150. Ethyl ether.—EtA′. (251° uncor.). S.G. $\underline{17\cdot5}$ 1·104. Amide.—$CH_2(OPh)CO.NH_2$. [102°]. From NH_3 and EtA′. Nitrile.—$CH_2(OPh)CN$. (237°). S.G. $\underline{17\cdot5}$ 1·09. From P_2O_5 and the amide. Thio-amide. — $CH_2(OPh)CS.NH_2$. [111°]. From the amide and alcoholic sulphide of ammonium. Anilide. — $CH_2(OPh)CO.NHPh$. [99°]. Formed by heating phenyl-glycollate of aniline to 150°.

Bromo-phenyl derivative $C_6H_4Br.O.CH_2.CO_2H$. *Bromo-phenyl-glycollic acid.* [154°]. Solidifies at 143°. Formed by saponifying its ether. Also from the phenyl derivative and Br. It forms dimetric prisms, v. sol. alcohol, hardly soluble in water. Salts.—NaA′ 2aq.—BaA'_2 1½aq. *Ethyl ether.*—Et′A. [59°]. Solidifies at 28°. From phenyl-glycollic ether (70g.) dissolved in CS_2 (140g.), cooled to 0°, and treated gradually with bromine (65g.) (Fritzsche, *J. pr.* [2] 20, 295). *Properties.*—Insoluble in water, crystallises from alcohol.

Chloro-phenyl derivative $C_6H_4Cl.O.CH_2.CO_2H$. [152°]. Formed from $C_6H_5.O.CH_2.CO_2H$ by successive treatment with PCl_5 and water (Michael, *J. pr.* [2] 35, 96). Prisms.

o-Nitro-phenyl derivative $(NO_2)C_6H_4O.CH_2.CO_2H$. [157°]. *Preparation.*—*o*-Nitrophenol (30g.), chloracetic acid (20g.) neutralised with strong NaOH are heated at 100° for 11 hours. The yield is fair (15g.) (A. Thate, *J.pr.* [2] 29, 148). *Properties.*—Yellowish-white pyramids (not regular octahedra). Doubly refracting. *Reactions.*—1. Reduced in alkaline solution by *sodium amalgam* to azoxy-, azo-, hydrazo-, and amido- phenyl-glycollic acid successively. The azo- acid $N_2(C_6H_4.O.CH_2.CO_2H)_2$ is crystalline [152°].—2. Reduced by *iron-filings* and *acetic acid* to amido-phenyl glycollic acid, or rather its anhydride $C_6H_4<\genfrac{}{}{0pt}{}{O.CH_2}{NH.CO}>$ [167°] (Thate, *J. pr.* [2] 25, 266). This anhydride is not affected by Ac_2O at 180°. When heated with zinc-dust it yields a very small quantity of a base C_8H_9NO (c. 200°) (Duparc, *B.* 20, 1942).—3. Reduced by *stannous chloride* and HCl to the anhydride of chloro-amido-phenyl-glyoxylic acid together with variable quantities of the anhydride of amido-phenyl-glycollic acid (Thate). Salts. — NaA′aq. — BaA′ 2aq. — CuA'_2 2½aq (Fritzsche, *J.pr.* [2] 20, 284).

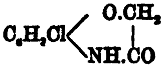
o-Nitro-phenyl derivative of the ethyl ether [2:1] $C_6H_4(NO_2).O.CH_2.CO_2Et$. [49°]. Colourless needles, sol. alcohol, ether, and benzene, insol. water (Duparc, *B.* 20, 1942). Reduced by tin and HCl to a base $C_8H_8ClNO_2$, which crystallises in long needles [195°], sol. alcohol and alkalis, insol. ether.

p-Nitro-phenyl derivative [4:1]$C_6H_4(NO_2)O.CH_2.CO_2H$. [183°]. From sodium *p*-nitro-phenol, sodium chloro-acetate, and caustic soda, each in concentrated solution. The mixture is evaporated, extracted with water, and treated with HCl. The acid is recrystallised from water (F.). Pale yellow plates. May be reduced to very unstable *p*-amido-phenyl-glycollic acid. Salts.—NaA′ 3aq.—BaA'_2 10aq.—CuA'_2 10aq.

o-Amido-phenyl derivative ×$NH_2.C_6H_4.O.CH_2.CO_2H$. *o-Amido-phenyl-glycollic acid.* This acid splits up at the moment of its formation into H_2O and an *anhydride*: $C_6H_4<\genfrac{}{}{0pt}{}{O.CH_2}{NH.CO}>$. [167°]. Solidifies at 144°. *Preparation.*—*o*-Nitro-phenyl-glycollic acid is reduced by iron filings and dilute (25 p.c.) acetic acid. The product is diluted, filtered, evaporated, and extracted with alcohol. The alcoholic extract is evaporated and the residue crystallised from water (A. Thate, *J. pr.* [2] 29, 178). *Properties.*—White cubes (from dilute alcohol), which nevertheless are doubly refracting. Sickle-shaped needles (from water), composed of small prisms joined in staircase fashion. Sol. ether, benzene, and alkalis. Can not be converted into a chloro- derivative by boiling with HCl. Boiled with alkalis the anhydride forms salts of amido-phenyl-glycollic acid. Salts.—KA′. Solutions of this salt give with $BaCl_2$ no pp. in the cold, a white pp. on boiling; with $Pb(OAc)_2$, a heavy white pp.; with $AgNO_3$, a copious white pp.; with $FeCl_3$, a dark brown pp.; with $CuSO_4$, a crystalline green pp. Acids ppt. the anhydride described above.—PbA'_2.—AgA′.

Chloro-o-amido-phenyl derivative ×$C_6H_2(NH_2)Cl.O.CH_2.CO_2H$. *Chloro-o-amido-phenyl-glycollic acid.*

Anhydride



$$C_6H_2Cl<\begin{array}{l}O.CH_2\\ \quad |\\ NH.CO\end{array}$$

[197°].

Preparation.—*o*-Nitro-phenyl-glycollic acid is digested at 100° with a solution of $SnCl_2$ and HCl

As soon as the liquid is filled with crystals it is allowed to cool, filtered, and recrystallised from alcohol (A. Thate, *J. pr.* [2] 29, 183). *Properties.*—White silky branching needles. insol. cold water, sl. sol. hot water, ether, and benzene, sol. alcohol. Salts.—KA′. Obtained by digesting the anhydride with KOH. Its solution gives with $BaCl_2$, no pp.; $Pb(OAc)_2$, white crystalline pp.; with $AgNO_3$, white flocculent pp.; $FeCl_3$, dark wine-red colour and, after a time, finely-divided cherry-red pp.; $CuSO_4$, yellowish-green pp.—NaA′.—AgA′.—PbA'_2.

Aldehydo-phenyl derivative v. vol. i. p. 110.

p-Tolyl derivative $C_9H_{10}O_3$ *i.e.* $CH_3.C_6H_4.O.CH_2.CO_2H$. [135°]. From chloro-acetic acid, *p*-cresol, and NaOHAq (Gabriel, *B.* 14, 923; Napolitano, *G.* 13, 73). Transparent prisms.—NaA′½aq: thin prisms.—NaA′aq: laminæ.—$BaA'_2$2aq: tables or prisms; sl. sol. cold water.—PbA'_2aq: laminæ.—AgA′.

o-Cumyl derivative $C_{11}H_{14}O_3$ *i.e.* [2:1]Pr.$C_6H_4.O.CH_2.CO_2H$. [130°]. From *o*-iso-propyl-phenol, chloro-acetic acid, and aqueous NaOH (Fileti, *G.* 16, 129). Needles (from water). Forms a crystalline Ba salt and amorphous Pb and Cu salts.—AgA′: white needles.

p-Cumyl derivative [4:1]Pr.$C_6H_4.O.CH_2.CO_2H$. [81°]. From *p*-iso-propyl-phenol, chloro-acetic acid, and NaOHAq (Spica, *G.* 10, 248). Silky needles, sol. water, v. sol. alcohol and ether. Unlike its *o*-isomeride, its solution is ppd. by $HgCl_2$, by $AuCl_3$, and by $PtCl_4$.—$BaA'_2$2aq: micaceous scales, m. sol. hot. water.—$PbA'_2$2aq: scales with hexagonal bases, sl. sol. water, sol. alcohol.

Thymyl derivative $C_3H_7.C_6H_3Me.O.CH_2.CO_2H$. [148°]. Solidifies at 132°. Formed by adding 30 g. of a solution of NaOH (S.G. 1·34) to a fused mixture of thymol (15 g.) and chloro-acetic acid (10 g.). Long needles (from alcohol). Sl. sol. water, v. sol. alcohol and ether. May be distilled with slight decomposition (Saarbach, *J. pr.* [2] 21, 159).—$BaA'_2$2aq: prisms.—PbA'_2.—AgA′: flocculent pp.

Ethyl ether of the thymyl derivative $C_3H_7.C_6H_3Me.O.CH_2.CO_2Et$. (290°).

Amide of the thymyl derivative $C_3H_7.C_6H_3Me.O.CH_2.CO.NH_2$. [97°]. V. sol. hot water, alcohol, and ether (Spica, *G.* 10, 245).

Carvacryl derivative $C_3H_7.C_6H_3Me.O.CH_2.CO_2H$. [149°]. Formed from carvacrol and chloro-acetic acid (Spica, *G.* 10, 245). White needles; sl. sol. water, v. sol. alcohol and ether.—$BaA'_2$4aq: prisms, sol. water.—PbA'_2: gummy mass (by ppn.), or minute prisms (from alcohol).—AgA′: minute needles.

Ethyl ether of the carvacryl derivative $C_3H_7.C_6H_3Me.O.CH_2.CO_2Et$. (289°). Oil.

Amide of the carvacryl derivative $C_3H_7.C_6H_3Me.O.CH_2.CO.NH_2$. [68°]. Sl. sol. cold water, sol. alcohol and ether.

Eugenyl derivative $C_3H_5.C_6H_3(OMe).O.CH_2.CO_2H$. [81°]. Formed by adding 30 g. of solution of NaOH (S.G. 1·34) to a fused mixture of chloro-acetic acid (10 g.) and eugenol (10 g.). Forms long satiny needles (from water). Not v. sol. water (L. Saarbach, *J. pr.* [2] 21, 158).—NaA′1½aq.

(α)-*Naphthyl derivative* $C_{10}H_7.O.CH_2.CO_2H$. [190°]. Formed by heating (α)-naphthol with chloro-acetic acid and gradually adding KOHAq (Spica, *G.* 16, 437). The product is diluted with water, acidified with HCl, and the pp. dissolved in aqueous ammonium carbonate to separate the unaltered (α)-naphthol. Small pale-red prisms, sl. sol. water, v. sol. ether and alcohol.—KA′aq: long acicular crystals, v. sol. water.—$PbA'_2$4½aq: white crystalline pp.—$BaA'_2$4½aq: white needles.—$MgA'_2$6½aq: pink scales. S. 2·46 at 28°.

Ethyl ether of the (α)-*Naphthyl derivative* $C_{10}H_7.O.CH_2.CO_2Et$. [173°]. Colourless crystals, sol. alcohol and ether. Alcoholic NH_3 gives a crystalline pp. of the amide $C_{10}H_7.O.CH_2.CONH_2$. [155°].

(β)-*Naphthyl derivative* $C_{10}H_7.O.CH_2.CO_2H$. [151°]. Prepared in like manner, using (β)-naphthol (Spica). Trimetric prisms; v. sl. sol. water, sol. alcohol and ether.—NH_4A': white unctuous scales [180°].—KA′.—$BaA'_2$3½aq: laminæ.—$(PbA'_2)_2PbO$: white crystalline pp.—$MgA'_2$3aq. S. ·62 at 26°.

Ethyl ether of the (β)-*naphthyl derivative* $C_{10}H_7.O.CH_2.CO_2Et$. [49°]. Large transparent scales; converted by alcoholic NH_3 into the amide $C_{10}H_7.O.CH_2.CO.NH_2$. [147°].

Tolylene derivative $Me.C_6H_3(O.CH_2.CO_2H)_2$. [217°]. From orcin (62 grms.), chloracetic acid (100 grms.) and caustic soda solution (540 grms. of 31 per cent.). The reaction is violent (Saarbach, *J. pr.* [2] 21, 162). Thin crystals (from water). Sl. sol. water, v. sol. alcohol and ether. Its solutions give an orange pp. with $FeCl_3$.—Na_2A'' 3aq. V. sol. water. Needles (from alcohol).—K_2A'' 3aq.—CaA″2aq. Ethyl ether.—Et_2A''. [107°]. Amide.—$Me.C_6H_3(O.CH_2.CONH_2)_2$. Amorphous.

Nitro-tolylene derivative $Me.C_6H_2(NO_2)(OCH_2.CO_2H)_2$. [140°]. Formed by the action of HNO_3 (S.G. 1·12) at 100° on the tolylene derivative. Crystallised from alcohol (Saarbach, *J. pr.* [2] 21, 168).

Pyrogallyl derivative $C_6H_3(OCH_2.CO_2H)_3$. [198°]. S. 1·3 at 15°. Formed by melting pyrogallol (12 pts.) with chloro-acetic acid (30 pts.) and then boiling with (200 pts. of) solution of soda (S.G. 1·3), and acidifying when cold (Giacosa, *J. pr.* [2] 19, 398).—K_3A'''.—KH_2A'' aq.

Diglycollic acid $C_4H_6O_5$ *i.e.* $O(CH_2.CO_2H)_2$. *Paramalic acid.* Mol. w. 134. [148°]. R_∞ 41·90 in a 14 p.c. aqueous solution (Kanonnikoff).

Formation.—1. Occurs in the preparation of glycollic acid from chloro-acetic acid by boiling with aqueous NaOH (Heintz, *P.* 109, 470), with alkaline earths, and with water and PbO or magnesia (Schreiber, *J. pr.* [2] 13, 436).—2. By oxidising di-ethylenic glycol with nitric acid or platinum-black (Wurtz, *C. R.* 51, 162).—3. A by-product in the preparation of glycollide by heating glycollic acid to 220° (Heintz, *P.* 115, 280, 452).

Properties.—Thick prisms (containing aq). Has no action on light. V. sol. water and alcohol. On distillation it gives formic paraldehyde and other products (Heintz, *A.* 128, 129). By heating with HIAq it is successively converted into glycollic and acetic acids. Fuming HClAq at 135° yields glycollic acid (Heintz, *A.*

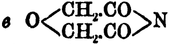
130, 257). Potash-fusion gives oxalic and acetic acids. PCl_5 forms chloro-acetyl chloride.

Salts.—The neutral alkaline salts are easily soluble in water, other diglycollates are but sparingly soluble.—NH_4HA'': long monoclinic prisms, insol. alcohol. S. 3·26 at 16°.—KHA'': trimetric crystals, sl. sol. water.—K_2A'': long deliquescent needles.—$NaHA''$: small tables, sl. sol. water, insol. alcohol.—$NaKA''2aq$: small tabular prisms with nacreous lustre, insol. alcohol. [100°].—Li_2A'' 5aq. S. 45 at 18·5°.—Li_2A'' $2\frac{1}{2}aq$ (Schreiber, *J. pr.* [2] 13, 436).—$BaH_2A''_2$: hard granular crystals.—BaA'' aq: white crystalline pp. S. ·17 at 100°.—CaA'' 6aq: long shining needles. Much less soluble than calcium glycollate.— CaA'' aq. — CaA'' 3aq. — CaA'' 4aq. — CaA'' 5aq.—SrA'' aq.—SrA'' 4aq: limpid, non-efflorescent crystals.—MgA'' 3aq: small prisms. —PbA'': minute crystals, sl. sol. water. — CuA'' $\frac{1}{2}aq$: blue crystalline pp. — ZnA''. — ZnA'' 3aq.—Ag_2A'': white granular pp.

Ethyl ether Et_2A''. (240°). From the silver salt and EtI (Heintz, *A.* 144, 95). Also from chloro-acetic ether, sodium glycollate, and Na_2CO_3 at 190° (Heintz, *A.* 147, 200). Heavy oil. Decomposed by boiling water into alcohol and diglycollic acid. Alcoholic NH_3 forms the amide $O(CH_2.CONH_2)_2$.

First Amide $NH_2.CO.CH_2.O.CH_2.CO_2H$. *Diglycollamic acid.* [135°]. Formed by heating the imide with baryta-water. Formed also by heating the second amide with water at 100° (Heintz, *A.* 128, 140). Trimetric prisms; m. sol. hot water, sl. sol. alcohol, nearly insol. ether.—BaA'_2aq: crystals; sol. water.

Second Amide $O(CH_2.CONH_2)_2$. From the ether and cold alcoholic NH_3. Trimetric prisms; v. e. sol. hot water, v. sl. sol. alcohol. HCl decomposes it into NH_3 and diglycollic acid.

Imide  $O<{CH_2.CO \atop CH_2.CO}>NH$. [142°]. S. 1·8 at 14°. Formed by distilling the preceding. Formed also by distilling acid ammonium diglycollate. Long needles.—$AgC_4H_4NO_3$: laminæ.

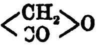
Triglycollic acid $C_6H_{12}O_8$. A syrupy acid, said to be formed by the action of Cl_2O on a mixture of Ac_2O and iodine (Schützenberger, *C. R.* 66, 1340).—$Ca_3A'''_2$.—$Ba_3A'''_2$ 2aq: prisms.

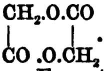
GLYCOLLIC ALDEHYDE $C_2H_4O_2$ *i.e.* $HO.CH_2.CHO$. It is doubtful whether this substance has been obtained. It is described by Abeljanz (*A.* 164, 213, 223) as a syrup, sol. ether, readily oxidised by Ag_2O to glycollic acid, and obtained by treating $CH_2Cl.CHCl.OEt$ with water at 115°. Abeljanz obtained the same body by treating $CH_2(OH).CHCl.OEt$ with conc. H_2SO_4.

Glycollic orthaldehyde $CH_2(OH).CH(OH)_2$.

Di-ethyl derivative $CH_2(OH).CH(OEt)_2$. (167°). V.D. 66·6 (calc. 67). From $CH_2Br.CH(OEt)_2$ by heating with alcoholic KOH for twelve hours at 170° (Pinner, *B.* 5, 150). Fragrant liquid. Decomposed by cold conc. H_2SO_4 and by gaseous HCl. Ac_2O at 120° yields a liquid resembling aldehyde, which may be glycollic aldehyde.

Tri-ethyl derivative $CH_2(OEt).CH(OEt)_2$. (164°) (P.); (168°) (L.). S.G. ^{21} ·892. From bromo-acetal and NaOEt at 160°. Also from $CH_2Cl.CHCl.OEt$ and NaOEt at 150° (Lieben, *A.* 146, 196). Fragrant liquid.

GLYCOLLIDE $C_2H_2O_2$ *i.e.*  $<{CH_2 \atop CO}>O$ or



. [220°] (N. a. T.); [180°] (D.).

Formation.—1. By heating glycollic acid to 240°, small quantities of diglycollic acid and of formic paraldehyde being formed at the same time (Heintz, *P.* 115, 452).—2. By heating anhydrous potassium chloro-acetate at 115° (Kekulé, *A.* 105, 288). If the crystallised salt be used most of the glycollide unites with water forming glycollic acid.—3. Glycollide was first obtained by heating tartronic acid to 180° as long as CO_2 escapes; after a few days the product solidifies, and is then washed with hot water (Dessaignes, *C. R.* 38, 46).

Preparation.—An alcoholic solution of chloro-acetic acid is added to a solution of sodium in 15 times its weight of dry alcohol; anhydrous chloro-acetate of sodium is ppd. and, after drying at 100°, this salt is gradually heated to 150° and kept for two days at that temperature. The product is freed from NaCl by washing with water, and may be dried at 200° (Norton a. Tscherniak, *C. R.* 86, 1332).

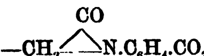
Properties.—Light white powder; neutral to litmus. Sl. sol. hot nitrobenzene. Dissolves in caustic potash, forming potassium glycollate. Ammonia forms the amide of glycollic acid. Ethylamine forms $HO.CH_2.CO.NHEt$. Aniline at 130° gives $HO.CH_2.CO.NHPh$. [108°].

Another anhydride of glycollic acid $C_4H_6O_5$. [130°]. Obtained by heating glycollic acid at 100° for a long time (Drechsel, *A.* 127, 154). Also from glycollic acid and the vapour of SO_3 (Fahlberg, *J. pr.* [2] 7, 336). Powder, insol. ether, alcohol, and cold water. Boiling water forms glycollic acid. Further heating converts this anhydride into glycollide.

GLYCOLLURIC ACID *v.* Hydantoic acid.

GLYCOLLYL-AMIDO-BENZOIC ACID $CH_2OH.CO.NH.C_6H_4.CO_2H$. [212°]. From *m*-amido-benzoic acid and glycollic acid at 150° (Pelizzari, *A.* 232, 153). Needles (from water). Sol. alcohol, sl. sol. ether.

Acetyl derivative $CH_2(OAc).CO.NH.C_6H_4.CO_2H$. [198°].

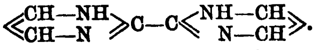
Anhydride.— $CH_2\overset{CO}{\wedge}N.C_6H_4.CO_2H$.[248°]. From $CH_2OH.CO.NH.C_6H_4.CO_2H$ by heat.

GLYCOLLYL-UREA *v.* Hydantoïn.

GLYCOLURIL *v.* Acetylene-urea, vol. i. p. 44.

GLYCOSE *v.* Sugar.

GLYCOSINE $C_6H_6N_4$ *i.e.*



. *Diglyoxaline.*

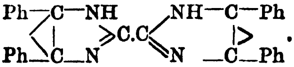
Formation.—1. By acting on glyoxal with ammonia (Debus, *A.* 107, 199; Japp a. Cleminshaw, *C. J.* 51, 553).—2. From tri-chloro-lactic acid and conc. NH_4Aq (Pinner, *B.* 17, 2000).

Properties.—White needles (from alcohol), v. sl. sol. alcohol.

Salts.—$B''_2H_2PtCl_6$: buff-coloured needles. —$B''H_2PtCl_6$.—$B''(H_2PtCl_6)_2$: deep-yellow crystals, stable at 120°.—$B''AgNO_3$ (Wyss, *B.* 10, 1375).—$B''(H_2C_2O_4)_2$: small nodules, m. sol. cold water.

Di-benzyl-glycosine $C_6H_4N_2(NC_7H_7)_2$. [145°]. Formed by heating glycosine with benzyl chloride and extracting the product with dilute hydric chloride (Japp a. Cleminshaw, *C. J.* 51, 555). Colourless plates, v. sol. benzene, sl. sol. petroleum ether.

Tetra-phenyl-glycosine



[above 300°].

Formed by acting on a mixture of benzil and glyoxal with ammonia (Japp a. Cleminshaw, *C. J.* 51, 553). White felted needles, m. sol. hot, sl. sol. cold, alcohol, v. sol. HOAc.

GLYCOSURIC ACID. [140°]. Occurs in urine in disease (Marshall, *Ar. Ph.* [3] 25, 593). Prisms; v. sol. water, alcohol, and ether, insol. benzene and light petroleum. Reduces Fehling's solution more strongly than glucose. An ethereal solution becomes red on evaporation. $FeCl_3$ gives a transient blue colour.

GLYCURONIC ACID $C_6H_{10}O_7$.

Formation.—1. Euxanthic acid (which occurs in puree or Indian yellow) is split up by heating with HCl or with dilute (3 p.c.) H_2SO_4 into glycuronic acid and euxanthone (Spiegel, *B.* 15, 1965; Külz, *Z. B.* 23, 475; Baeyer, *A.* 155, 257; Thierfelder, *H.* 11, 388). The decomposition is best effected by water at 125°.—2. By boiling (α)- or (β)- camphoglycuronic acid with dilute (5 p.c.) HCl (Schmiedeberg a. Meyer, *H.* 3, 422).—3. By boiling urochloralic acid with dilute H_2SO_4 (Mering, *H.* 6, 489).—4. When a rabbit is treated with *tert*-amyl alcohol its urine contains 'di-methyl-ethyl-carbinol-glycuronic' acid $C_{11}H_{20}O_7$, which is split up by boiling dilute H_2SO_4 into *tert*-amyl alcohol and glycuronic acid. *Tert*-butyl alcohol acts in like manner (Thierfelder a. Mering, *H.* 9, 515).

Properties.—Syrupy acid, v. sol. alcohol. On evaporation of its solution, or even on standing, it changes to the crystalline anhydride. Gives on oxidation camphoric and formic acids. Bromine converts it into saccharic acid (Thierfelder, *B.* 19, 3148). Sodium-amalgam reduces it to gluconic acid. Its K salt dissolved in 90 p.c. alcohol reacts with aniline forming $NPh{:}C_6H_9O_6K$, the potassium salt of the 'anilide of glucose' [177°]. *m*-Tolylene-diamine forms, in like manner, $C_7H_6(N{:}C_6H_9O_6K)_2$. Conc. KOHAq decomposes glycuronic acid, forming oxalic acid, pyrocatechin, and a little protocatechuic acid. Glycuronic acid gives lactic and acetic acid when fermented in presence of cheese and chalk.—KA': needles.—BaA'_2: amorphous, v. sol. water.

Anhydride $C_6H_8O_6$. [167°]. $[\alpha]_D=19{\cdot}25°$ at 18°. Monoclinic tables, with sweet taste. V. e. sol. water, insol. alcohol. Dextrorotatory. Reduces hot Fehling's solution. ·989 pts. reduce as much as 1 pt. of glucose. Hinders the ppn. of cupric hydroxide by alkalis.

Benzoyl derivative $C_6H_8Bz_2O_7$. [107°]. Obtained by treating the acid (1 mol.) with BzCl (9 mols.) and NaOH (12 mols.) in a 10 p.c. solution (Thierfelder, *H.* 13, 275). V. sol. alcohol. Reduces Fehling's solution.

Phenyl-hydrazide $C_{42}H_{48}N_{10}O_{10}$. [115°]. From the K salt and phenyl-hydrazine mixture. Yellow needles.

GLYCYPHYLLIN $C_{21}H_{24}O_9$. The sweet principle of *Smilax glycyphylla*. Extracted from the leaves and stem by alcohol, the extract being evaporated and the residue dissolved in water and extracted with ether (Wright a. Rennie, *C. J.* 39, 237; 49, 857). Crystallises from wet ether with 3aq, and from water in prisms containing 4½aq. Has no definite melting-point. Sl. sol. cold water, v. sol. hot water and alcohol, m. sol. ether. Insol. chloroform, benzene, and light petroleum. Dissolves in aqueous KOH, the solution turning red in air. Does not reduce Fehling's solution. Is ppd. by lead subacetate. Boiling dilute H_2SO_4 converts it into phloretin $C_{15}H_{14}O_5$ and isodulcite $C_6H_{14}O_6$.

GLYCYRRHIZIC ACID $C_{44}H_{63}NO_{18}$. Occurs, probably in combination with ammonia, in the liquorice root (*Glycyrrhiza glabra* and *G. echinata*) (Vogel, jun., *J. pr.* 28, 1; Lade, *A.* 59, 224; Gorup-Besanez, *A.* 118, 236; Hirsh, *Ph.* [3] 1, 749; Roussin, *Ar. Ph.* [3] 8, 156; Robiquet, *A. Ch.* [4] 72, 143; Sestini, *G.* 8, 454; Habermann, *A.* 197, 105). Occurs also in large quantities in the rhizomes of *Polypodium vulgare* and of *P. semipennatifidum*, both of which ferns are used as substitutes for liquorice (Guignet, *C. R.* 100, 151). Habermann finds in liquorice, besides glycyrrhizic acid, a brown resin, which yields *p*-oxy-benzoic acid when fused with potash, and an amorphous bitter substance $C_{36}H_{57}NO_{13}$, sl. sol. water and ether, v. sol. HOAc and aqueous Na_2CO_3.

Preparation.—1. The dried and powdered root is extracted with dilute acetic acid; alcohol is added; and the filtrate evaporated to a syrup and washed with water (Guignet).—2. The root is extracted with boiling water containing a little milk of lime; the concentrated extract is ppd. with HOAc. The gelatinous pp. is dissolved in 50 p.c. alcohol, deodorised by charcoal, and evaporated at 100° (Sestini).—3. Commercial 'Glycyrrhizin ammoniacale' is boiled with glacial acetic acid and filtered while hot. The acid ammonium salt then crystallises from the filtrate (Habermann). The acid may be obtained by conversion into the lead salt and decomposing by H_2S.

Properties.—Gelatinous mass (from hot aqueous solution). When dry it forms an amorphous solid, which swells up in cold water. V. sl. sol. ether and alcohol, sol. boiling HOAc. Turns brown at 100°. It has a sweet taste and an acid reaction. Expels CO_2 from $CaCO_3$ suspended in hot water. Reduces Fehling's solution on heating. Boiling dilute acids split it up into glycyrrhetin and parasaccharic acid $C_6H_{10}O_8$.

Salts.—NH_4H_2A''': laminæ (from alcohol or HOAc); prepared as above. Insol. ether, sl. sol. alcohol, v. e. sol. boiling water. Separates from dilute alcohol or hot water in a gelatinous form.—$(NH_4)_3A'''$: amorphous gummy mass, v. sol. water, insol. alcohol. Has an intensely sweet taste.—KH_2A''': crystalline grains. Swells up in cold water, forming a jelly; v. sol. hot water, v. sl. sol. alcohol. Extremely sweet.—K_3A''': yellowish amorphous mass; v. sol. water, v. sl. sol. alcohol. From its solution in HOAc the salt KH_2A''' crystallises out.—$Ba_3A'''_2$: flocculent pp.—$Pb_3A'''_2$: yellowish-brown mass, sl. sol. water, insol. alcohol, sol. HOAc.

Glycyrrhetin $C_{32}H_{47}NO_4$. [200°]. Formed by boiling glycyrrhizic acid with dilute acids (Habermann, *B.* 10, 870; Griessmeyer, *D. P. J.* 209, 228). Crystalline powder; has no taste. Insol. water, ether, and alkalis; sol. alcohol, HOAc, and H_2SO_4. Does not give *p*-oxy-benzoic acid on potash-fusion (Habermann; *cf.* Weselsky a. Benedikt, *B.* 9, 1158).

Di-acetyl derivative $C_{32}H_{45}Ac_2NO_4$. [217°]. From glycyrrhetin and AcCl. Crystalline powder; insol. water. Gives on oxidation amorphous $C_{32}H_{47}NO_6$.

Bromo-glycyrrhetin $C_{32}H_{46}BrNO_4$. From glycyrrhetin and Br in HOAc. Crystalline powder, insol. water and alcohol, sl. sol. HOAc, v. sol. $CHCl_3$.

Nitro-glycyrrhetin $C_{32}H_{46}(NO_2)NO_4$. Formed by treating a solution of glycyrrhetin in HOAc with HNO_3. Powder.

GLYOXAL $C_2H_2O_2$ *i.e.* CHO.CHO. *Oxalic aldehyde.* Mol. w. 58. Formed by the action of nitric acid on alcohol (Debus, *A.* 102, 20; 107, 199; 110, 316; 118, 253), aldehyde or paraldehyde (Lubavin, *B.* 8, 768).

Preparation.—1. Obtained from the mother-liquor in the preparation of glyoxylic acid by the slow oxidation of alcohol by HNO_3; the liquid is mixed with several times its volume of conc. $NaHSO_3Aq$. The crystalline compound is subsequently decomposed by dilute H_2SO_4.—2. Paraldehyde (25 g.) is mixed with water (25 g.); HNO_3 (20 c.c. of S.G. 1·37) is poured in so as to form a lower layer of liquid, and below this again fuming HNO_3 (1 c.c.) is introduced. After a week the liquid is evaporated at 100°, taken up in water, neutralised by $CaCO_3$, glycollic and glyoxylic acids ppd. by lead subacetate, filtered, freed from excess of lime by oxalic acid, again filtered, and evaporated (De Forcrand, *Bl.* [2] 41, 240).

Properties.—Amorphous, slightly deliquescent mass. After drying at 100° it contains *x*aq and is v. e. sol. water, but after drying at 120° it is v. sl. sol. cold water. At 170° it is partially converted into glycollide. It is v. e. sol. alcohol and ether. It reduces ammoniacal $AgNO_3$, forming a mirror. Water at 150° converts two-thirds of it into glycollic acid.

Reactions.—1. A small quantity of very dilute *nitric acid* oxidises it to glyoxylic acid; a larger quantity of nitric acid forms oxalic acid. 2. Aqueous *alkalis* convert it into glycollic acid, even in the cold.—3. Cold aqueous KCy forms a black substance.—4. *Ammonium cyanate* forms glycocoll (Lubavin, *J. R.* 1882, 281; *C. J.* 44, 178).—5. Conc. aqueous NH_3 forms, in the cold, glycosine $C_6H_6N_4$ and glyoxaline $C_3H_4N_2$.—6. An alcoholic solution of *aniline* forms $C_{28}H_{24}N_4$ (Schiff, *B.* 11, 831), a crystalline base, insol. water, sol. alcohol, forming the platinochloride $B'_2H_2PtCl_6$ and the nitro- derivatives $C_{28}H_{20}(NO_2)_4N_4$ and $C_{28}H_{16}(NO_2)_8N_4$.—7. *Aniline* heated with the compound of glyoxal with $NaHSO_3$ forms the anilide of phenyl-amido-acetic acid $NHPh.CH_2.CO.NHPh$ [113°] (Hinsberg, *B.* 21, 110).—8. (α)- and (β)-*Naphthylamine* heated with the compound of glyoxal with $NaHSO_3$ form the sodium salt of the sulphonate of (α)- and (β)-naphthoxindole $C_{10}H_6\left<\begin{array}{c}NH\\CH_2\end{array}\right>CO$ (Hinsberg).—9. *Aceto-acetic ether* and conc. aqueous $ZnCl_2$ form methyl-carboxy-furfuryl-acetic acid and an ether $C_{14}H_{18}O_6$ [139°] which crystallises in plates, v. sol. most menstrua, insol. alkalis, and on saponification gives an acid [75°] (Polonowsky, *A.* 246, 17).—10. Gaseous HCl passed through a mixture of glyoxal and *ethylene mercaptan* forms $\begin{array}{l}CH_2.S\\ |\\ CH_2.S\end{array}\!\!>CH.CH<\!\!\begin{array}{l}S.CH_2\\ \quad|\\ S.CH_2\end{array}$ [133°] (Fasbender, *B.* 21, 1476).—11. *Malonic ether* (2 mols.) acted on by glyoxal (1 mol.) and zinc chloride gives rise to di-oxy-butane tetra-carboxylic ether $(CO_2Et)_2.CH.CH(OH).CH(OH).CH(CO_2Et)_2$ (Polonowski, *A.* 246, 1).—12. *Aceto-acetic ether* and conc. $ZnCl_2Aq$ forms di-methyl-furfurane di-carboxylic acid $O\left<\begin{array}{l}C(CH_2.CO_2H):CH\\CMe=C(CO_2H)\end{array}\right>$, a compound $C_{14}H_{18}O_6$ [139°], and oily $O\left<\begin{array}{l}C(CHAc.CO_2Et):CH\\CMe=C(CO_2Et)\end{array}\right>$.—13. Aqueous di-methyl-urea evaporated with glyoxal and a little HCl forms tetra-methyl-glycolurile $CO\left<\begin{array}{c}NMe.CH.NMe\\ |\\ NMe.CH.NMe\end{array}\right>CO$ [217°] (Franchimont a. Klobbie, *R. T. C.* 7, 236).

Combinations $C_2H_2O_2(NH_4HSO_3)_2$: prisms, v. sol. water, insol. alcohol (De Forcrand, *C. R.* 100, 642).—$C_2H_2O_2(NaHSO_3)_2$ aq: small crystals, v. sol. water, insol. alcohol.—$C_2H_2O_2(KHSO_3)_2$: prisms (De Forcrand, *C. R.* 98, 1537).—$C_2H_2O_2Ba(HSO_3)_2\ 2\frac{1}{2}aq$: concentrically-grouped masses. S. ·85 at 18°.

Diphenyl hydrazide $HC(N_2HPh).CH(N_2HPh)$. [170°]. Got by warming glyoxal or its compound with $NaHSO_3$ with excess of aqueous phenylhydrazine hydrochloride and sodic acetate (Pickel, *A.* 232, 231; Fischer, *B.* 17, 575). Formed also by the action of phenyl-hydrazine on tri-chloro-lactic acid (Pinner, *B.* 17, 2001). Rosettes of slender needles or plates (from alcohol). Nearly insol. water and light petroleum, sol. benzene and chloroform. By warming with alcoholic $FeCl_3$ it is oxidised to the 'osotetrazone' $\left<\begin{array}{l}CH.N:NPh\\CH.N:NPh\end{array}\right.$ [152°] which crystallises from alcohol in dark red plates (Von Pechmann, *B.* 21, 2751).

Salt.—B'HCl. [156°]. Saponified by water.

Phenyl-ethyl-hydrazide $HC(N_2EtPh).CH(N_2EtPh)$. [149°]. Formed by adding the compound of glyoxal with $NaHSO_3$ to a dilute solution of phenyl-ethyl-hydrazine in HClAq (Elbers, *A.* 227, 340). Crystals (from alcohol); v. sol. benzene and chloroform, m. sol. ether and cold alcohol.

Oxim $C_2H_4N_2O_2$ *i.e.* HC(NOH).CH(NOH). *Glyoxim.* [178°]. Formed by the action of hydroxylamine on glyoxal (Wittenberg a. Meyer, *B.* 16, 505). Formed also by the action of hydroxylamine upon tri-chloro-lactic acid (Pinner, *B.* 17, 2001). Sublimable. Colourless trimetric tables. Sol. hot water, alcohol, and ether. Boiled with aqueous acids it is resolved into its constituents. By heating with acetic anhydride it yields cyanogen (Lach, *B.* 17, 1573). Phenyl-hydrazine added to its alcoholic solution forms an addition-compound $C_2H_4N_2O_2N_2H_3Ph$ [110°], which crystallises from alcohol in white scales, insol. water (Polonowsky, *B.* 21, 182).—$AgC_2H_3N_2O_2$: white powder.

Di-acetyl derivative $C_2H_2(NOAc)_2$: [120°]; colourless crystals. By further heating with acetic anhydride it yields cyanogen (Lach, *B.* 17, 1573).

Reference.—Chloro-glyoxim.

Paraglyoxal hydrate $C_{12}H_{14}O_{13}$ *i.e.* $(C_2H_2O_2)_6H_2O$. Formed by passing HCl into a solution of glyoxal (1 vol.) in HOAc (5 vols.) (Schiff, *G.* 4, 16; *A.* 172, 1). Powder, insol. water, ether, benzene, and chloroform, sl. sol. boiling alcohol. Prolonged boiling with water converts it into glycollic acid. Caustic alkalis also form glycollates. Boiling Ac_2O forms amorphous insoluble $C_{12}H_{13}AcO_{13}$. BzCl gives amorphous $C_{12}H_{13}BzO_{13}$.

Orthoglyoxal $CH(OH)_2.CH(OH)_2$. *Oxalic orthaldehyde.*

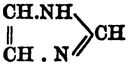
Ethyl derivative $CH(OEt)_2.CH(OEt)_2$. (c. 180°). Formed by the action of NaOEt upon di-chloro-acetal $CHCl_2.CH(OEt)_2$ (Pinner, *B.* 5, 147). Oil. Entirely destroyed by strong acids.

GLYOXAL-AMYLINE *v.* Butyl-glyoxaline.

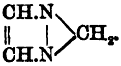
GLYOXAL-ISOBUTYLINE *v.* Propyl-glyoxaline.

GLYOXAL-ETHYLINE *v.* Methyl-glyoxaline.

GLYOXALINE $C_3H_4N_2$ *i.e.*



(Japp, *C. J.* 43, 17) or



Methylene-acetylene-azine. [89°]. (255°). V.D. 2·35 (calc. 2·26). Formed, together with glycosine, by the action of strong aqueous ammonia on glyoxal (Debus, *A.* 107, 204; Lubavin, *J. R.* 7, 254; Wyss, *B.* 9, 1543; 10, 1365; Wallach, *B.* 15, 645). Formed also by the simultaneous action of formic aldehyde and NH_3 on glyoxal (Radziszewsky, *B.* 15, 1495).

Preparation.—Glyoxal is treated very gradually with ammonia in slight excess, the temperature being kept down. Glycosine then separates as a brown powder, and the filtered solution contains the glyoxaline together with ammonia, chiefly as acetate. This liquid is boiled with milk of lime to expel the ammonia, then evaporated to a syrup, treated with absolute alcohol to separate mineral salts, and filtered; the residue is strongly pressed to separate as much as possible of the liquid; and the whole of this liquid is distilled from a wide-necked retort. After one rectification the glyoxaline is perfectly pure, and solidifies to a radiate, dazzling-white crystalline mass (Wyss).

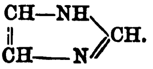
Properties.—Thick nacreous prisms, v. sol. water, alcohol, and ether; is not deliquescent. Has an alkaline reaction. Not attacked by chromic acid. Not affected by reducing agents, by Ac_2O, by AcCl, or by BzCl.

Reactions.—1. $KMnO_4$ oxidises it to formic acid and CO_2.—2. EtBr forms $C_3H_3EtN_2HBr$ and $C_3H_3EtN_2EtBr$.—3. Benzyl chloride forms in like manner $C_3H_3(C_7H_7)N_2C_7H_7Cl$ (Wyss).—4. The hydrochloride treated with $AgNO_2$ forms a nitroso-derivative.—5. *Hydrogen peroxide* forms oxamide (Radziszewsky, *B.* 17, 1289).—6. *Bromine* added to an aqueous solution of glyoxaline forms tri-bromo-glyoxaline $C_3HBr_3N_2$, which crystallises from water in needles. It is v. sl. sol. cold water, v. sol. alcohol, sl. sol. ether. It dissolves in alkalis and is reppd. by acids, behaving as an acid. Its silver salt $C_3AgBr_3N_2$ is converted by MeI into $C_3MeBr_3N_2$, which may be reduced by sodium-amalgam to methyl-glyoxaline.

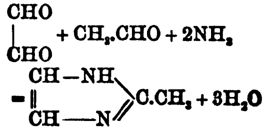
Salts. — $B''_2H_2PtCl_6$: orange-red prisms (from hot water) (Debus). — $B''_2H_2PtCl_6$ xaq (Wallach).—$B''_2H_2ZnCl_4$: very soluble crystals.—$B''H_2C_2O_4$: prisms. S. 2·06 at 19°.—$C_3AgH_3N_2$: white amorphous pp.; insol. cold water.

References. — Methyl-, Methyl-ethyl-, Ethyl-, Propyl-, Butyl-, and Isoamyl-glyoxalines.

GLYOXALINES. These compounds are derivatives of glyoxaline



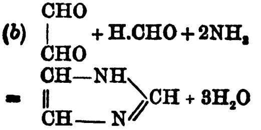
General modes of formation.—They are formed by the condensation of compounds containing the dicarbonyl-group —CO.CO— (α-diketones and α-dialdehydes) with aldehydes and ammonia jointly, the reaction taking place according to Equation II. of the general reactions of this class (*v.* vol. i. p. 465). Thus glyoxal, aldehyde, and ammonia yield methyl-glyoxaline:—



(Radziszewski, *B.* 15, 2706; Japp, *C. J.* 1883, 197; *v.* also under Equation II., vol. i. p. 465).

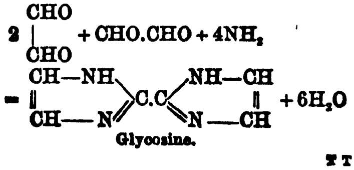
The aldehyde necessary for the reaction is sometimes furnished by the preliminary hydrolysis of a portion of the dicarbonyl-compound. Thus the reaction discovered by Debus (*T.* 148, 209), in which glyoxaline itself is obtained by treating glyoxal with ammonia, is supposed to occur in two stages:

(*a*) $CHO.CHO + H_2O = H.COOH + H.CHO$
Formic aldehyde.



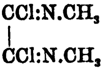
(Radziszewski, *B.* 15, 1495; Japp, *B.* 15, 2419). In a similar manner lophine (triphenyl-glyoxaline) is obtained from benzil and ammonia, benzoic aldehyde being first formed (*v.* vol. i. pp. 467–8); and trimethyl-glyoxaline from diacetyl and ammonia (Von Pechmann, *B.* 21, 1417).

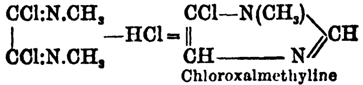
Glyoxal also reacts with ammonia without first undergoing hydrolysis, yielding glycosine (D.), which is a *diglyoxalyline.* In this case 3 mols. of glyoxal take part in the reaction, one of these exercising the function of the aldehyde (here a dialdehyde) and the other two that of the dicarbonyl-compound in the aldehyde-diketone-ammonia condensations:



Glycosine.

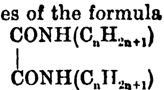
(Japp a. Cleminshaw, *C. J.* 1887, 553; *cf.* also formation of *tetraphenylglycosine*, vol. i. p. 465).

Wallach has shown that chlorinated glyoxalines are formed by the action of phosphorus pentachloride on *s*-dialkyloxamides (*A.* 184, 33; 214, 278; *B.* 16, 546; *v.* also Japp, *B.* 15, 2418; *C. J.* 1883, 197). In the first stage an imido-chloride is formed: thus *s*-dimethyloxamide would yield  $\begin{array}{l}\text{CCl:N.CH}_3\\|\\\text{CCl:N.CH}_3\end{array}$. (The imido-chloride was not isolated in this particular case, but the corresponding diethyl-compound was obtained.) The imido-chloride parts, either spontaneously or on gently heating, with the elements of hydrochloric acid, yielding a chlorinated glyoxaline. Thus with dimethyloximidochloride:



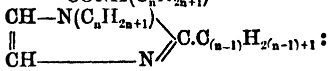
Chloroxalmethyline (Methylchlorglyoxaline).

The mechanism of this reaction is not understood (Wallach, *B.* 16, 546). By heating with hydriodic acid and amorphous phosphorus, the compound is reduced to the corresponding 'oxalmethyline' (tertiary methylglyoxaline). The name 'oxalines' was given to this class of compounds to denote their connection with oxalic acid, before it was recognised that they were derivatives of glyoxaline. The general formula of the 'oxalines' derived from *s*-dialkyloxamides of the formula

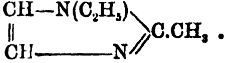


$$\begin{array}{l}\text{CONH(C}_n\text{H}_{2n+1})\\|\\\text{CONH(C}_n\text{H}_{2n+1})\end{array}$$

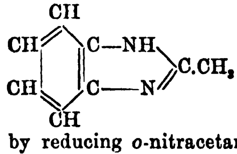
is

:

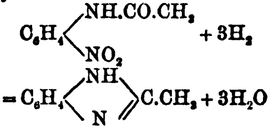
thus 'oxalethyline' from *s*-diethyloxamide is

.

Another class of glyoxalines are the anhydrobases derived from orthodiamines: thus anhydracetdiamidobenzene (ethenylphenylenediamine)

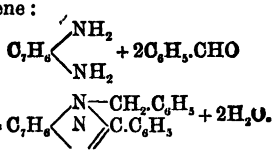


is obtained by reducing *o*-nitracetanilide with tin and hydrochloric acid:

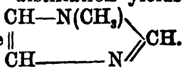
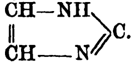
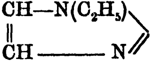


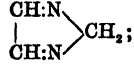
(Hübner, *A.* 209, 353). The same compounds may be prepared from the orthodiamines by heating them with carboxylic acids: thus *o*-diamidobenzene and acetic acid yield the foregoing anhydracetdiamidobenzene (Ladenburg, *B.* 8, 677).

Ladenburg (*B.* 11, 590) obtained by the condensation of aldehydes with orthodiamines a class of stable bases to which he gave the name of 'aldehydines.' Hinsberg (*B.* 19, 2025) has shown that these compounds are tertiary anhydrobases. Thus (1, 3, 4)-tolylenediamine and benzaldehyde form benzyl-anhydrobenzdiamidotoluene:

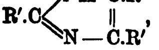


The aldehydines, therefore, also belong to the class of the glyoxalines.

General properties and reactions.—Glyoxaline and most of its true homologues are solid compounds; but the derivatives in which the alkyl-group is attached to nitrogen are generally liquid. The glyoxalines are monacid bases, and behave towards alkyl iodides like secondary bases; thus glyoxaline yields with methyl iodide the compound $C_3H_3(CH_3)N_2,CH_3I$, which by treatment with moist silver oxide is converted into an ammonium hydroxide; this by distillation yields the tertiary methylglyoxaline . The conversion of the secondary glyoxalines into tertiary compounds by the introduction of an alkyl-group lowers the boiling-point: thus glyoxaline boils at 255°, tertiary methyl-glyoxaline at 197°-199°. When the tertiary alkyl-glyoxalines are distilled through a red-hot tube, the alkyl leaves the nitrogen and attaches itself to the 'meso' carbon atom: *i.e.* the carbon atom which is situated between the two nitrogen atoms. In this way the foregoing tertiary methylglyoxaline may be converted into *meso*-methylglyoxaline , identical with the compound (*v. supra*) obtained from glyoxal, aldehyde, and ammonia (Wallach, *B.* 16, 542; Radziszewski, *B.* 15, 2706). By oxidation with hydrogen peroxide, glyoxaline and its *meso*-homologues yield oxamide; whilst the tertiary alkyl-glyoxalines and their *meso*-homologues yield monalkyl oxamides: thus oxalethyline  gives ethyloxamide (Radziszewski, *B.* 17, 1290).

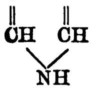
It has not been found possible to replace the imidic hydrogen in glyoxal and its homologues by acid radicles, and from this Radziszewski (*B.* 15, 1494 and 2706; 16, 492) has argued that glyoxaline contains two tertiary nitrogen atoms, formulating it thus: ; but the results of alkylation and of the oxidation of the alkyl- derivatives prove conclusively that imidic hydrogen is present, and far outweigh this merely negative evidence (Japp, *B.* 15, 2419; 16, 284; Wallach, *B.* 16, 538). Besides, glyoxaline gives off ammonia when heated with aniline hydrochloride, and sulphuretted hydrogen when its aqueous solution is heated with carbon disulphide—reactions which a tertiary base would hardly exhibit (Wallach, *B.* 16, 539).

Classification.—The glyoxalines are amidines in which two hydrogen atoms—one in the amido- and one in the imido-group—have been replaced by the dyad group $—CR'=CR'—$ so as to convert the complex $R'.C\begin{smallmatrix}NH_2\\NH\end{smallmatrix}$ into

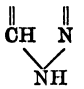


, forming a closed-chain compound. Thus glyoxaline itself is formamidine $CH\begin{smallmatrix}NH_2\\NH\end{smallmatrix}$ into which the group $—CH=CH—$ has been introduced. The amidines, like the glyoxalines, are monacid bases.

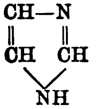
Glyoxaline is one of the two possible compounds which may be derived from pyrrhole as pyridine is derived from benzene—by replacing a CH- group by triadic nitrogen:



Pyrrhole.



Pyrazole.



Glyoxaline.

F. R. J.

GLYOXAL ŒNANTHYLINE *v.* HEXYL GLYOXALINE.

GLYOXALIC ACID *v.* GLYOXYLIC ACID.

GLYOXAL-PROPYLINE *v.* ETHYL-GLYOXALINE.

GLYOXIM *v.* *Di-oxim* of GLYOXAL.

GLYOXYLIC ACID $C_2H_3O_2$ *i.e.* $H.CO.CO_2H$. *Glyoxalic acid.*

Occurrence.—In the leaves and unripe fruits of many plants (Brunner, *B.* 19, 595).

Formation.—1. By the action of nitric acid upon alcohol, glycol, glyoxal, or glycerin (Debus, *P. M.* [4] 12, 361; *A.* 100, 1; 102, 28; 110, 316; Heintz, *A.* 152, 325).—2. By boiling silver di-bromo-acetate with water (Perkin, *C. J.* 21, 197; 32, 90).—3. By heating di-chloro-acetic ether with water (Fischer a. Geuther, *J. Z.* 1, 47).—4. By boiling silver di-chloro-acetate with water (Beckurts a. Otto, *B.* 14, 531).—5. By heating silver bromo-glycollate with ether in sealed tubes there is formed an amorphous substance (? glyoxylic anhydride) which is converted by boiling water into glyoxylic acid (Perkin a. Duppa, *C. J.* 21, 197).—6. By heating dry silver di-chloro-acetate at 80° there is formed an oil $C_4H_2Cl_2O_4$ which is split up by water into glyoxylic and di-chloro-acetic acids (Beckurts a. Otto, *B.* 14, 586).

Preparation.—1. Di-bromo-acetic acid (1 pt.) is heated with water (10 pts.) for 24 hours at 135° (Grimaux, *Bl.* [2] 26, 483).—2. 220 g. of alcohol of 80 p.c. are poured into a tall narrow flask capable of holding about 1½lb. of water; 100 g. of water are introduced below the alcohol by means of a funnel having its neck finely drawn out; and below this are poured 200 g. of red fuming nitric acid, so that the three liquids may remain one above the other and mix as little as possible at first. The whole is left for six or eight days, at a temperature of 20°-22° C., till the liquids have become completely mixed, and the resulting nitrite of ethyl has volatilised. The residual liquid—containing nitric, acetic and formic acids, compound ethers, glyoxal and other aldehydes, glycollic acid and glyoxylic acid—is evaporated to a syrup over the water-bath in portions of 20 to 30 g. each; the residues, containing oxalic, glycollic, and glyoxylic acids, together with the less volatile aldehydes, are dissolved in small quantities of water; the united solutions are neutralised with chalk; the neutral liquid is mixed with an equal volume of alcohol; and the resulting pp. of calcium-salts pressed and repeatedly boiled with water. The aqueous extract yields crystals of glyoxylate of calcium, and a further quantity of this salt may be obtained by concentrating the mother-liquor. The subsequent mother-liquors yield a double salt of glycollate and glyoxylate of calcium, and the last contain glycollate of calcium (Debus). 7,500 c.c. alcohol yield 308 g. glyoxylic acid (Böttinger, *A.* 198, 207).

Properties.—Thick syrup (S.G. 1·3), which crystallises over H_2SO_4 in trimetric prisms containing aq, and which may therefore be looked upon as orthoglyoxylic acid $CH(OH)_2.CO_2H$. V. sol. water. When strongly heated it gives off acid vapours, leaving a carbonaceous residue. Volatile with steam. Its calcium salt reduces boiling ammoniacal silver nitrate forming a mirror. Glyoxylic acid forms compounds with $NaHSO_3$, with H_2S, and with NH_3. An aqueous solution of calcium glyoxylate is ppd. by excess of lime-water, and the pp. $Ca_3(C_4H_5O_8)_2$ is converted by boiling water into a mixture of glycollate and oxalate. When a solution of calcium glyoxylate is mixed with aniline oxalate, and the liquid is filtered from calcium oxalate, a colourless solution is obtained, which, when boiled or even when left to itself for a few hours, deposits a bright orange-coloured precipitate (Perkin a. Duppa). Aniline (75 g.) acts upon syrupy glyoxylic acid (42 g.) forming $PhN:CH.CO_2H$, and its aniline salt $PhN:CH.CO_2NPhH_3$; the aniline salt is converted by long boiling with water into a red powder $C_{16}H_{12}N_2O_3$ (Böttinger, *A.* 198, 222). The barium salt $(PhN:CH.CO_2)_2Ba$ is v. e. sol. water, insol. alcohol. Phenyl-hydrazine solution gives a pp. in an aqueous solution of glyoxylic acid.

Reactions.—1. *Zinc* is dissolved by glyoxylic acid, the acid being reduced to glycollic acid.—2. *Nitric acid* oxidises it to oxalic acid.—3. PBr_5 forms di-bromo-acetyl bromide (Perkin a. Duppa, *C. J.* 21, 197).—4. PCl_5 acting on the potassium salt KA'aq forms di-chloro-acetyl chloride, KCl, di-chloro-acetic acid, and free glyoxylic acid $CHO.CO_2H$ (Beckurts a. Otto, *B.* 14, 1619).—5. Boiling aqueous KOH forms glycollic and oxalic acids (Böttinger, *B.* 13, 1932).—6. By treatment with potassium cyanide and boiling the product with baryta there is formed tartronic acid $CO_2H.CH(OH).CO_2H$. — 7. *Tolylene-o-*di-amine on boiling with calcium glyoxylate forms a crystalline acid $C_7H_6\begin{smallmatrix}N\\NH\end{smallmatrix}C.CO_2H$aq? sl. sol. water, v. sol. alcohol, and decomposing at 160° (Hinsberg, *A.* 237, 358).

Salts.—With the exception of the ammonium and potassium salts, these might equally well be described as salts of ortho-glyoxylic acid. —NH_4A': small prisms, v. sol. water (Perkin; *cf.* Engel, *C. R.* 98, 628). Its concentrated solution turns yellow when boiled. Gives pps. with $AgNO_3$, with $Pb(OAc)_2$, and with $CuSO_4$.—KA': ppd. as an oil by adding alcohol to its aqueous solution; solidifies after a time. Insol. alcohol.—BaA'_2 4aq: small white crystals; partly resolved by boiling water into glycollate and oxalate.—CaA'_2 2aq;

thin needles or hard prisms. S. ·57 at 8°. It does not give off water at 170°, but at 180° it gives off water and CO_2, leaving glycollate and carbonate.—$Ca_3(C_4H_5O_8)_2$.—CaA'_2 4aq: gelatinous pp. got by adding alcohol to the aqueous solution.—$(CaA'_2)_3(NH_3)_4$ 2aq.—$(CaA'_2)_3(NH_3)_4$: formed by adding ammonia to an aqueous solution of calcium glyoxylate at 50°.—Pb(OH)A'.—Zn(OH)A' aq: white crystalline pp. got by adding a conc. solution of calcium glyoxylate to zinc acetate.—AgA' aq: white crystalline powder; sl. sol. cold water.—$(AgA')_4(NH_3)_3$ (Debus).

Combinations with bisulphites.—$NaA'NaHSO_3$: formed by adding a conc. solution of $NaHSO_3$ to one of glyoxylic acid. Crystals, v. sol. water.—$(CaA'_2)_2Ca(SO_3H)_2$ 10aq: formed by passing SO_2 into water, in which calcium glyoxylate is suspended.—**Calcium glyoxylate and glycollate** $(Ca(C_2HO_3)_2)_2Ca(C_2H_3O_3)_2$ 4aq.—**Calcium glyoxylate and lactate** $Ca(C_2HO_3)_2Ca(C_3H_5O_3)_2$ aq.

Phenyl-hydrazide $C_6H_5NH.N:CH.CO_2H$. Formed as a pp. of fine yellow needles by adding a solution of phenyl-hydrazine hydrochloride to an aqueous solution of glyoxylic acid (Fischer, *B.* 17, 577). Yellow needles. Decomposes at 137°. Sol. alcohol and hot water.

Phenyl ethyl hydrazide $C_6H_5NEt.N:CH.CO_2H$. Ppd. by adding phenyl-ethyl-hydrazine hydrochloride to a dilute solution of calcium glyoxylate acidified by HCl (Elbers, *A.* 227, 340). White needles, m. sol. hot water, v. sol. alcohol and acetic acid.

Orthoglyoxylic acid $CH(OH)_2.CO_2H$. This is perhaps the true formula of glyoxylic acid.

Di-ethyl-derivative $CH(OEt)_2.CO_2H$.

Formation.—1. From tetra-chloro-ethylene and NaOEt at 100°-120° (Geuther a. Fischer, *J.* 1864, 316).—2. By boiling di-chloro-acetic acid (18 pts.) with alcohol (90 pts.), in which sodium (10 pts.) has been dissolved (Schreiber, *Z.* 1870, 167).

Properties.—Unstable oil; split up by boiling with HCl into alcohol and glyoxylic acid.—$Ba(C_6H_{11}O_4)_2$: deliquescent amorphous mass.—$AgC_6H_{11}O_4$: m. sol. water.

Ethyl ether of the di-ethyl derivative $CH(OEt)_2.CO_2Et$. (199° cor.). S.G. $\underline{13}$ ·994. Formed from $CH(OEt)_2.CO_2Na$ and EtI at 120° (Schreiber, *Z.* 1870, 167). Formed also by heating glyoxylic acid with alcohol at 120° (Perkin, *B.* 8, 188). Obtained by passing HCl into a solution of HCy in dry alcohol (Pinner a. Klein, *B.* 11, 1475).

Isobutyl ether of the di-isobutyl derivative $CH(OC_4H_9)_2CO_2.C_4H_9$. (251°). Formed by passing HCl into a solution of dry HCy in isobutyl alcohol (P. a. K.). Oil. After saponification it gives the salt $CH(OC_4H_9)_2.CO_2Ag$, which crystallises in small needles, sl. sol. cold water.

Amide of the di-ethyl derivative $CH(OEt)_2.CONH_2$. [77°]. (Schreiber, *Z.* 1870, 168); [82°] (Pinner a. Klein, *B.* 11, 1477). From $CH(OEt)_2.CO_2Et$ and cold alcoholic NH_3. Tables or needles (by sublimation). V. sol. water and alcohol).

Amide of the di-isobutyl derivative $CH(OC_4H_9)_2.CONH_2$. [c. 44°]. Crystalline (P. a. K.).

Reference.—Chloro-glyoxylic ether.

GLYOXYLYL CYANIDE ×CHO.CO.CN.

Phenyl-hydrazide $CHO.C(N_2HPh).CN$. [161°]. Formed by the action of a concentrated solution of hydrochloric acid upon the di-oxim of the phenyl-hydrazide of mesoxalic aldehyde $CH(NOH).C(N_2HPh).CH(NOH)$ (Von Pechmann a. Wehsarg, *B.* 21, 3000). Sulphur-yellow needles, insol. water, sol. other solvents. Decomposed on melting. Conc. H_2SO_4 forms a yellow solution not affected by $FeCl_3$. Boiling HIAq liberates aniline. When its dilute alkaline solution is poured into a neutral solution of diazobenzene chloride there is formed $C_9H_6N_3O(N_2Ph)$ [163°] which crystallises from alcohol in brown plates, insol. alkalis.

Oxim of the phenyl-hydrazide $CH(NOH).C(N_2HPh).CN$. [240°]. Formed by treating the preceding with hydroxylamine hydrochloride in alcoholic solution. Lemon-yellow difficultly soluble needles, decomposed by fusion. Its solution in H_2SO_4 is not effected by $FeCl_3$.

Di-phenyl hydrazide $CH(N_2HPh).C(N_2HPh).CN$. [161°]. Formed by the action of phenyl-hydrazine on a hot alcoholic solution of the monophenylhydrazide $CHO.C(N_2HPh).CN$ (Von Pechmann a. Wehsarg, *B.* 21, 3000). Orange-red needles, decomposed on fusion; sol. alcohol and HOAc, sl. sol. most other solvents. The solution in H_2SO_4 is not affected by $FeCl_3$. $FeCl_3$ or $K_2Cr_2O_7$ acting on its solution in dilute HOAc forms the 'osotetrazone' $\left\langle\begin{matrix}CH:N.NPh\\CCy:N.NPh\end{matrix}\right\rangle$, which crystallises in bronzed hair-like needles, melting, with decomposition, at 137°.

The corresponding acid $CH(N_2HPh).C(N_2HPh).CO_2H$ [203°] is formed by treating di-bromo-pyruvic acid with phenyl hydrazine (Nastvogel, *A.* 248, 85). *p*-Tolyl hydrazine and (*a*)-naphthyl hydrazine form similar acids, melting at 188° and 196° respectively.

Phenyl-methyl-hydrazide $CHO.C(N_2MePh).CN$. [114°]. Prepared from $CH(NOH).C(N_2MePh).CH(NOH)$ by treating its solution in acetone with conc. HClAq. Converted by phenyl-hydrazine in acetic acid solution into $CH(N_2HPh).C(N_2MePh).CN$ [181°], which forms yellow plates. Aniline produces the compound $CH(NPh).C(N_2MePh).CN$, which crystallises from alcohol in slender yellow needles [151°].

Oxim of the phenyl-methyl-hydrazide $CH(NOH).C(N_2MePh).CN$. [178°]. Formed from the preceding and hydroxylamine. Yellow needles. Boiling acetic anhydride forms $CH(NOAc).C(N_2MePh).CN$, which crystallises from alcohol in yellow needles [122°].

GLYOXYLYL UREA $C_3H_4N_2O_3$ *i.e.* $NH_2.CO.NH.CO.CHO$. The potassium salt is formed with evolution of CO_2, on adding acetic acid to a solution of the potassium salt of oxonic acid $C_4H_3N_3O_4$ (Medicus, *A.* 175, 230; *B.* 9, 1162; 10, 544). Thick shining needles, sl. sol. cold, v. sol. hot, water.—KA': crystalline powder.—AgA': amorphous powder.

Isomeride *v.* Allanturic acid.

GNOSCOPINE $C_{34}H_{36}N_2O_{11}$. [233°]. S. (cold alcohol) ·07. An alkaloid obtained from the mother-liquors in the purification of narceine

(T. a. H. Smith, *Ph.* [3] 9, 82). Sol. chloroform and CS_2, sl. sol. benzene. Insol. aqueous or alcoholic NaOH. Dissolves in acids. The solution in conc. H_2SO_4 is yellow, turned crimson by a trace of KNO_3. A solution of the hydrochloride gives a buff-coloured pp. with platinic chloride.

GOA POWDER *v.* CHRYSAROBIN, p. 173.

GOLD. Au (*Aurum*). At. w. 196·85 (Thorpe a. Laurie, *C. J.* 51, 565, 866). At. w. 196·64 (Krüss, *B.* 20, 205, 2365). Mol. w. unknown. [1045°] (Violle, *C. R.* 92, 866); [1240°] (Riemsdyck, *C. N.* 20, 23; for other determinations *v.* Carnelley's *Melting and Boiling-point Tables*). S.G. $\frac{17.5°}{17.5°}$ 19·3 to 19·33 (G. Rose, *P.* 73, 1). S.H. 0°–100° ·0316 (Violle, *C. R.* 89, 702); 12°–98° ·03244 (Regnault, *A. Ch.* [2] 73, 1). C.E. at 40° ·00001443 (Fizeau, *C. R.* 68, 1125); 0° to 100° ·0000147 (Matthiessen, *Pr.* 15, 220). T.C. 53·2 (Ag = 100) (Wiedmann a. Franz, *P. M.* [4] 7, 33). E.C. at 0° = 43·84 to 44·62 (Hg at 0° = 1) (Matthiessen a. Von Bose, *T.* 152, 1). For description of emission-spectrum *v.* de Boisbaudran's *Spectres Lumineux*.

Gold has been known and used from prehistoric times. The names by which the metal is known in different languages generally express the property of brightness. The method of separating gold by amalgamating it with mercury is fully described by Pliny.

Occurrence.—Gold is found native, generally more or less alloyed with Ag. It occurs in the crystalline, the compact metamorphic, the trachytic, and trap, rocks, and in alluvial soils. The greatest quantity is obtained from alluvial deposits formed by the disintegration of ancient auriferous strata. Gold is most abundant in Europe in Hungary and Transylvania; but it occurs in small quantities in very many primitive mountains or in the sands of rivers issuing from such mountains, *e.g.* in the southern slopes of the Alps, in North Wales, in the Scottish Highlands, and in the Ural mountains. It is also found in fair quantities in Brazil and Chili, and other parts of S. America; abundantly in California, and parts of Australia, and in British Columbia. The purest specimens of native gold contain about 99 p.c. Au. The Californian gold averages from 87·5 to 88·5 p.c., and the Australian from 96 to 96·6 p.c. Au.

Extraction of Gold.—(1) By washing away the earthy particles with water. This is effected on a large scale in California by means of a head of water rushing through a pipe with a narrow nozzle. Sometimes the sands of an auriferous stream are washed in a wooden *cradle*, which is rocked by hand. (2) By amalgamation. The richer gold-containing rocks are crushed and mixed with mercury, whereby an amalgam of Au and Hg is formed; this amalgam is separated from the earthy matter and heated in specially constructed iron retorts; the gold remains and the Hg is recovered. Poorer ores are washed before amalgamation. (3) By smelting. Ores which contain small quantities of Au mixed with Cu and Pb, and sulphides, are sometimes roasted, and then mixed with quartz and smelted; the mass is powdered and treated with dilute H_2SO_4Aq; the residue is mixed with fresh quantities of ore and the treatment is repeated; when a fair quantity of Au has accumulated in the residue it is boiled with conc. H_2SO_4 to dissolve Ag, Cu, &c., and the insoluble matter is subjected to a process of *parting*. (4) By wet processes. The principal process is that based on converting Au into soluble $AuCl_3$ by treatment with Cl. The ore is thoroughly roasted to remove S, As, and Sb; the moistened residue is then treated with Cl which must be free from HCl; on addition of warm water, the $AuCl_3$ dissolves; the Au is ppd. generally by ferrous sulphate. In whatever way the Au has been separated it is usually still alloyed with Ag; this is separated by *parting*. Sufficient Ag is added to ensure the presence of 5 parts Ag to 2 parts Au; the alloy is granulated and treated with pure nitric acid in which the Ag dissolves, while the Au remains insoluble. Or the alloy, which should contain from 19 to 25 p.c. Au, is treated with hot conc. H_2SO_4; Ag dissolves and Au is insoluble. The treatment with HNO_3 or H_2SO_4 is repeated; the Au is washed and melted with borax and nitre. For details of these and other processes of gold extraction *v.* DICTIONARY OF TECHNICAL CHEMISTRY.

Preparation.—Au may be obtained from any alloy with Ag in which it is present by treating with a mixture of 2 measures of conc. HClAq and 1 of conc. HNO_3, filtering, evaporating at 100° until acid vapours are no longer evolved, dissolving the residue in warm water acidulated with HCl, filtering, and ppg. Au by addition of $FeSO_4Aq$. Or an alloy of Ag and Au, or of Ag, Cu, and Au, containing not more than 20 p.c. Au, may be granulated, heated with 2½ times its weight of H_2SO_4Aq S.G. 1·815 in a Pt vessel as long as SO_2 is evolved, boiled with a little more H_2SO_4Aq S.G. 1·65, and allowed to settle; the liquid is then poured off and the treatment with H_2SO_4 S.G. 1·815 is repeated once or twice; finally the residual Au is washed and dried. Krüss (*A.* 238, 30) prepared pure Au, for his determination of the atomic weight, by dissolving the purest commercial Au in *aqua regia*, evaporating to dryness at 100° with HCl, dissolving in water, diluting largely, and filtering; he then ppd. the Au (1) by SO_2, followed by washing with HClAq and water, drying at 180°, digesting with conc. H_2SO_4 in a Pt dish, washing with hot water, drying, fusing (in Pt) with $KHSO_4$ (to remove Pd), then fusing with KNO_3 (to remove Ir), redissolving in *aqua regia*, and reppg. by SO_2. By method (2) the Au was ppd. from the dilute $AuCl_3$ solution by oxalic acid; in method (3) the pptant. used was $FeCl_2$. In each case the Au was washed, dissolved in *aqua regia*, and reppd. by SO_2, again washed, and redissolved in *aqua regia*, and finally ppd. by oxalic acid. Thorpe a. Laurie (*C. J.* 51, 570) prepared pure Au, from old assay cornets, by dissolving in *aqua regia*, evaporating to remove excess of nitric acid, diluting with much water, allowing to settle for several weeks, pouring off from traces of AgCl, ppg. by SO_2, and boiling the pp. with water till every trace of Cl was removed.

Properties.—Au is the only metal of a yellow colour; in thin sheets it appears greenish by transmitted light. Au ppd. from solution by SO_2Aq or $FeSO_4Aq$ appears as a lustreless, brown-yellow to reddish, powder. Au crystallises in regular forms chiefly octahedra and dodecahedra.

Au is softer than Ag but harder than Sn. When pure, Au is the most malleable of all metals, sheets ·0001 mm. thick have been obtained. The ductility of Au is nearly limitless; a grain of Au has been drawn into a wire 500 ft. long. Au is not oxidised by heating in air; it is volatilised and perhaps partially oxidised when a strong electric current is passed through thin leaves or wires. Insoluble in HNO_3, conc. HClAq, or H_2SO_4; dissolved by *aqua regia*. Cl and Br combine direct with Au forming $AuCl_3$ and $AuBr_3$ respectively; the metal also combines directly with P; and it forms alloys with several metals (*v. infra*, Alloys). Compounds of Au are generally easily decomposed by heat, yielding Au. *Purple of Cassius* is probably a mixture of SnO_2 with Au (*v.* Tin, oxides of).

Gold is distinctly and decidedly metallic in its physical properties; but in many of its chemical relations it belongs to the non-metals. The composition of the aurous compounds Au_2O, Au_2S, AuCl, &c., marks the resemblance between Au and the alkali metals; the solubility in water of Au_2S and Au_2O emphasises this resemblance. The marked instability of the salts of Au, the acidic character of the hydroxide AuO_3H_3, of the sulphides Au_2S and AuS, and the existence of the acids $HAuCl_4$ and $HAuBr_4$, mark the analogy between Au and the non-metals. In the classification based on the periodic law, Au is placed both in Group I. which contains the alkali metals, and in Group VIII. which contains the metals Fe Ni Co and also the Pt metals. Au is the first member of series 11, in which it is followed by Hg, Tl, Pb, and Bi; these four elements are decidedly metallic, but both Pb and Tl form salts in which they play the part of negative elements. (For a further discussion of the chemical relations of Au *v.* Copper group of elements, p. 250.)

The atomic weight of Au has been determined very carefully by Thorpe a. Laurie, from (1) the ratio Au:KBr, and (2) the ratio Au:AgBr; the salt used was $KAuBr_4$ (*C. J.* 51, 565, 866). Krüss (*B.* 20, 205, 2365) has also determined the at. w. from analyses of $KAuBr_4$, and also of $AuCl_3$. (For an account of older determinations *v.* paper of Thorpe a. Laurie.)

Allotropic form of Gold.—According to Thomsen (*Th.* 3, 398) the Au ppd. by SO_2Aq from solutions of $AuBr_3$ differs from that ppd. from $AuCl_3Aq$; the thermal measurements of the two reduction-processes show, according to Thomsen, that Au ppd. from $AuBr_3$ possesses energy equal to 3,210 gram-units of heat, per 197 grams of gold, more than the Au ppd. from $AuCl_3$.

Gold, alloys of. Gold alloys with most metals. The alloys which are of most technical importance are those with *copper* and *silver*. Pure Au is too soft for making jewellery, watches, coins, &c.; alloying it with Cu increases the hardness, and produces a redder colour than that of pure Au. Alloying with Ag gives a lighter colour. Alloys of Au with Cu and Ag are more fusible than pure Au. The standard coinage of the United Kingdom is 11 Au to 1 Cu. Au forms *amalgams* with Hg. By dissolving 1 pt. Au in about 1,000 pts. Hg, pressing through chamois leather, and treating the residue with HNO_3Aq, a solid amalgam approximating to the composition Au_8Hg is said to be obtained (Henry, *P. M.* (4) 9, 468). An amalgam, approximately Au_2Hg_3, is found native in California. Another amalgam, approximately $Ag_2Au_8Hg_{10}$, is found in New Granada. The pasty amalgam of 2 pts. Au with 1 pt. Hg is sometimes used for *gilding* articles of copper and bronze. The surface of the article is cleaned thoroughly by heating and immersing in dilute H_2SO_4Aq, it is then amalgamated by rubbing with $Hg(NO_3)_2Aq$, and then pressed on the pasty amalgam of Au; the Hg is then driven off by heat, and the surface is polished. Copper may also be gilded by immersion in boiling $AuCl_3Aq$ to which an alkaline carbonate has been added. The process of gilding generally consists in depositing Au from solution of the cyanide in KCNAq by an electric current, the object to be gilded being made the negative pole, while the positive consists of a bar of gold (*v.* Dictionary of technical chemistry).

Gold bromides. Aurous bromide AuBr, and auric bromide $AuBr_3$, have been isolated, and, according to Thomsen, a third bromide $AuBr_2$ also exists; as none of the bromides has been gasified, the above formulæ may or may not be molecular. Thomsen gives the following thermal data (*Th.* 3, 412) [Au, Br] = −80; [Au, Br^3] = 8,850; [Au, Br^3, Aq] = 5,090; [$AuBr^3$, Aq] = −3,760; [$AuBr^3Aq$, 3HClAq] = 4,280. $AuBr_3$ combines with HBr to form $HAuBr_4$ (*v. infra*).

Aurous bromide AuBr (or Au_2Br_2). $HAuBr_4.5H_2O$ (*v. infra*) is placed in a porcelain basin, the bottom, but not the sides, of which is gently heated; the salt melts and then evolves H_2O and HBr; the dish is then kept in a drying oven at 115° until the colour is yellowish-grey (Thomsen, *Th.* 3, 390). AuBr is described by Thomsen as a greyish-yellow body with a talc-like appearance, unchanged in air and insoluble in water; decomposed somewhat above 115° into Br and Au; reacts with HBrAq to form $HAuBr_4$ and Au.

Auro-auric bromide $AuBr_2$ (or $AuBr.AuBr_3$). According to Thomsen (*Th.* 3, 386), this compound is produced by treating Au which has been reduced by SO_2Aq and dried at 170° with excess of Br, removing the excess of Br by tilting the vessel, powdering the residue, and again treating with a little Br. Thomsen describes $AuBr_2$ as a compact, almost black, non-deliquescent, mass; at c. 115° it is decomposed to AuBr and Br; it dissolves slowly in water to form AuBr and $AuBr_3$; it is decomposed rapidly by acids and also by anhydrous ether into $AuBr_3$, which dissolves, and a residue, probably AuBr, which slowly decomposes to $AuBr_3$ and Au. According to Krüss a. Schmidt (*B.* 20, 2634) $AuBr_2$ does not exist.

Auric bromide $AuBr_3$. Ppd. Au is dissolved in BrAq, or better in HBrAq containing HNO_3, and the solution is evaporated at a low temperature. Thomsen (*Th.* 3, 387) recommends to treat $AuBr_2$ with anhydrous ether, which is kept cold by the passage through it of a current of air, and then to evaporate the conc. solution thus obtained by sucking a rapid current of air through it (if temperature is not kept low, reduction of $AuBr_3$ takes place), to allow the residue to stand over time until dry, then to powder and dry at 70°. $AuBr_3$ is a dark-brown, non-deliquescent, powder; soluble in water and ether; the solutions when conc. are nearly black. $AuBr_3Aq$ is partially reduced by boiling; SO_2Aq forms AuBr and then Au. $AuBr_3$ combines with HBr to form $HAuBr_4$ (*v. infra*).

Auro-bromhydric acid $HAuBr_4.5H_2O$ (*Aurobromic acid. Bromo-auric acid. Hydrogen bromo-aurate*). Finely divided Au is treated with excess of Br; when the reaction is completed, HBrAq S.G. 1·38 is added in the proportion of 100 g. to every 100 g. Au used, and then enough Br is added to dissolve completely all the Au; the liquid is poured into a porcelain dish which is allowed to stand in a cool place. Large, dark, vermillion-red crystals soon separate; after an hour or so the mother liquor is poured off, and the crystals are dried at a temperature not exceeding 20°. The crystals melt at 27°; they are unchanged in ordinary air. $HAuBr_4Aq$ is reduced to Au by SO_2Aq (*Th.* 3, 389). Thomsen (*Th.* 3, 411) gives the thermal data: $[AuBr^3Aq,HBrAq] = 7,700$; $[AuBr^3, HBrAq] = 3,880$; $[AuBr^3, HBr, 5H^2O] = 35,280$; $[Au, Br^3, HBrAq] = 12,790$; $[HAuBr^4Aq, 4HClAq] = -510$; $[3AuBr, HBrAq] = 3,650$; $[AuBr^4Aq, 2SO^2Aq] = 61,790$; $[HAuBr^4. 5H_2O, Aq] = -11,400$.

Aurobromate of potassium $KAuBr_4$. *Potassium bromo-aurate.* Monoclinic crystals; $a:b:c = {\cdot}79688:1:{\cdot}361$; $\beta = 85° \; 34' \; 2''$ (Schottländer, *A.* 240, 346). Prepared by dissolving a mixture of finely-divided Au and KBr, in the ratio Au:KBr, in excess of Br with addition of a considerable quantity of water, evaporating, and crystallising from water (Thorpe a. Laurie, *C. J.* 51, 571). The salt is decomposed by heat to Au and KBr. According to Krüss (*B.* 20, 2365) $KAuBr_4$ cannot be obtained perfectly free from traces of Au; but this is denied by Thorpe a. Laurie (*C. J.* 51, 866). The salt in solution is very easily partially reduced.

Gold chlorides. Two chlorides AuCl and $AuCl_3$ certainly exist; Thomsen says that a third chloride, $AuCl_2$, is also produced by the reaction between Au and Cl; this is denied by Krüss, but re-asserted by Thomsen. The formulæ AuCl, $AuCl_2$, and $AuCl_3$ are the simplest that can be given; but as the compounds have not been gasified these formulæ are not necessarily molecular.

Aurous chloride AuCl. Best prepared according to Thomsen (*Th.* 3, 386) by heating $AuCl_3$ to 185°. Yellowish-white powder; insol. water, but decomposed by water, quickly on heating, to $AuCl_3Aq$ and Au. $[Au, Cl] = 5,810$; $[3AuCl, HClAq] = 4,980$ (*Th.* 3, 411).

Auro-auric chloride $AuCl_2$ (or $AuCl.AuCl_3$). Thomsen (*Th.* 3, 383) describes this compound as a hard, dark red, very hygroscopic, solid; decomposed by water to AuCl and $AuCl_3Aq$; decomposes at c. 250° giving some $AuCl_3$; prepared by leading dry Cl over Au ppd. by SO_2Aq from $AuCl_3Aq$, the reaction being started by gentle heating and then allowed to proceed until all the Au is changed to $AuCl_2$ (*Th.* 3, 383; *v.* also Thomsen, *J. pr.* [2] 37, 105). Krüss a. Schmidt (*B.* 20, 2634; and also *J. pr.* [2] 38, 77) assert that the products of the action of Cl on Au are a mixture of Au and $AuCl_3$, and that no $AuCl_2$ is produced.

Krüss (*B.* 20, 211) says that when finely-divided Au is heated in dry Cl to 140° auro-auric chloride is produced; at 180°-190° this is decomposed with formation of AuCl and a little $AuCl_3$; at 220°-230° a little more $AuCl_3$ is obtained and the AuCl decomposes to Au and Cl, and that the Au thus produced remains unchanged in the Cl; on cooling these reactions are reversed. But in a subsequent memoir Krüss a. Schmidt say that the only products of the reaction of Au with Cl are AuCl and $AuCl_3$, and finally $AuCl_3$ and Au.

Auric chloride $AuCl_3$. Formed by dissolving Au in *aqua regia*, evaporating, and crystallising, and drying on a porous tile over conc. H_2SO_4 for several days. A purer product is obtained by evaporating the solution in *aqua regia* to dryness, heating the residue to 185° so long as Cl is evolved, decomposing the AuCl thus formed by a very little hot water, allowing to settle, decanting from Au, and evaporating to dryness the conc. $AuCl_3Aq$ thus obtained over a flame arranged so that the bottom and not the sides of the vessel is kept hot; when the residue is heated to 150° pure $AuCl_3$ is obtained. Thomsen (*Th.* 3, 384) recommends to treat $AuCl_2$ instead of AuCl with water in the manner directed. If conc. $AuCl_3Aq$ is evaporated to the crystallising point, and then allowed to stand in dry air, large orange crystals of the hydrate $AuCl_3.2H_2O$ separate; these are dehydrated by standing on a porous tile over conc. H_2SO_4 for some days (*Th.* 3, 386). $AuCl_3$ is also formed by heating finely-divided Au in Cl (*v. supra*). Lindet (*C. R.* 101, 1492) recommends to heat Au in Cl in presence of $AsCl_3$, $SiCl_4$, $SbCl_5$, $SnCl_4$, or $TiCl_4$; $AuCl_3$ is formed and dissolves in the other chloride, but separates in crystals on cooling.

Auric chloride crystallises in large red-brown leaflets; it is very deliquescent, and dissolves in water with production of heat. $AuCl_3Aq$ is easily reduced; Au is ppd. by P, many metals, $FeSO_4$, $H_2C_2O_4$, As_2O_3, Sb_2O_3, and by organic matter; reduction also occurs by the action of light (*v.* Foussereau, *C. R.* 103, 248); $AuCl_3Aq$ is not reduced by *pure* NaOH, but if organic matter is present reduction occurs (Krüss, *A.* 237, 274). $AuCl_3$ dissolves in hot $AsCl_3$, $SiCl_4$, $SbCl_5$, $SnCl_4$, and $TiCl_4$, but separates again on cooling. When Au is heated with S_2Cl_2 the compound $AuCl_3.SCl_4$ is formed; and when Au is heated with $SeCl_4$ dissolved in molten $AsCl_3$, and Cl is passed in, the compound $AuCl_3.SeCl_4$ is produced (Lindet, *C. R.* 101, 1492). $AuCl_3$ combines with HCl to form $HAuCl_4$ (*v. infra*). HBr reacts with $AuCl_3$ to form $HAuCl_4$, $HAuBr_4$, and HCl (*Th.* 3, 410). Thomsen (*Th.* 3, 411) gives the thermal data:—$[Au, Cl^3] = 22,820$; $[AuCl^3, Aq] = 4,450$; $[Au, Cl^3, Aq] = 27,270$; $[AuCl^3.2H^2O,Aq] = -1,690$; $[AuCl^3Aq, 4HBrAq] = 15,210$.

Auro-chlorhydric acid $HAuCl_4.4H_2O$. (*Aurochloric acid. Chloro-auric acid. Hydrogen chloro-aurate*). Long yellow needles, formed by dissolving Au in *aqua regia*, adding a large excess of HCl, evaporating to a syrup, and allowing to crystallise. Also by dissolving $AuCl_3Aq$ in HClAq and evaporating; in dry air $HAuCl_4.3H_2O$ is formed (*Th.* 3, 407). $HAuCl_4$ is also formed, along with $HAuBr_4$ and HCl, when excess of HBrAq is added to $AuCl_3Aq$ (*Th.* 3, 410). $[AuCl^3Aq, HClAq] = 4,530$; $[Au, Cl^3, HClAq] = 31,800$; $[AuCl^3, HCl, 4H^2O] = 32,130$; $[AuCl^3Aq, 4HBrAq] = 15,210$;

$[HAuCl^4Aq, 4HBrAq] = 13{,}800$; $[HAuCl^4.4H^2O,Aq] = -5{,}830$; $[HAuCl^4.3H^2O,Aq] = -8{,}550$.

Ammonium auro-chlorate, $(NH_4)AuCl_4$ (*Ammonium chloro-aurate*). By dissolving NH_4Cl in $AuCl_3Aq$ strongly acidified with HCl, and evaporating, monoclinic yellow tablets are obtained, having the composition $4NH_4AuCl_4.5H_2O$; if these are dissolved in water and re-crystallised rhombic plates are formed $2NH_4AuCl_4.5H_2O$. Both salts are dehydrated at 100°.

Potassium auro-chlorate or *chloro-aurate*, $KAuCl_4$. Formed similarly to the NH_4 salt; crystallises in yellow needles, $2KAuCl_4.H_2O$; the crystals effloresce in the air; when heated they melt with evolution of Cl, and the liquid solidifies to $KAuCl_2$.

Sodium auro-chlorate or *chloro-aurate*, $NaAuCl_4.2H_2O$. Formed similarly to the NH_4 salt.

Aurochlorates of Ba, Cd, Ca, Co, Mg, Mn, Ni, Sr, and Zn have been obtained by Von Bonsdorff (*P.* 17, 261; 33, 64).

Gold cyanides; and **double cyanides**, also **auricyanides**, *v.* pp. 331–2.

Gold, fulminating, *v.* AURIC OXIDE, *infra.*

Gold hydroxides *v.* GOLD, OXIDES AND HYDROXIDES OF, *infra.*

Gold iodides. Two are known, AuI and AuI_3.

Aurous iodide AuI. A citron-yellow powder, insol. cold, sl. sol. hot, water. Formed by adding HIAq to Au_2O_3, I being set free in the reaction; or by adding an equivalent quantity of KI in solution, little by little, to $AuCl_3Aq$ ($AuCl_3Aq + 3KIAq = AuI + 3KClAq + 2I$). Decomposed at 120° to Au and I; decomposed by KOHAq with ppn. of Au. $[Au,I] = -5{,}520$ (*Th.* 3, 412).

Auric iodide AuI_3. A dark-green pp. formed by adding $AuCl_3Aq$, little by little, to KIAq. When less than $AuCl_3$ is added to 4KI a dark-green liquid is formed, and then a pp. which dissolves on shaking; on then adding a little more $AuCl_3Aq$ the liquid is decolourised and AuI_3 is ppd. (probably (1) $4KIAq + AuCl_3Aq = 3KClAq + KAuI_4Aq$ and (2) $3KAuI_4Aq + AuCl_3Aq = 3KClAq + 4AuI_3$). AuI_3 is very unstable; exposed to the air it changes to AuI. It combines with HI, but little is known of the properties of the compound; with KI it forms $KAuI_4$.

Potassium auro-iodate or *iodo-aurate* $KAuI_4$. Black, lustrous, four-sided prisms; formed by dissolving AuI_3 in KIAq, or by mixing AuI_3 and KIAq in the ratio AuI_3:4KI, and allowing the liquid to crystallise. Soluble, with partial decomposition, in water. Decomposed by heat to Au and KI (*cf.* Johnston, *P. M.* [3] 9, 266). $[AuCl^3Aq,3KIAq] = 45{,}660$ (*Th.* 3, 411).

Gold, oxides and hydroxides of. Three oxides of Au have been isolated: *aurous oxide* Au_2O, *auro-auric oxide* AuO, and *auric oxide* Au_2O_3. Aurylic hydroxide AuO.OH (or $Au_2O_2(OH)_2$) has been obtained, and perhaps one or two other hydroxides intermediate between AuO.OH and AuO_3H_3. There is still doubt as to the isolation of auric hydroxide AuO_3H_3. Oxides of Au containing more O than Au_2O_3 have been described, but according to Krüss none of these exists (*v.* Krüss, *B.* 19, 2541; references to older papers are given by Krüss). The hydrate $Au_2O.2H_2O$ described by Raschig (*A.* 235, 341) does not exist according to Krüss.

Aurous oxide Au_2O. This oxide is best prepared by adding SO_2Aq, drop by drop, to $KAuBr_4Aq$ kept at 0° until the red colour just disappears, pouring off the liquid, warming the residual AuBr with KOHAq, washing the ppd. hydrated Au_2O with boiling water, and drying over P_2O_5 (Krüss, *B.* 19, 2543). Au_2O is a greyish-violet solid; when freshly ppd. it is somewhat soluble in cold water, but is ppd. on boiling; also slightly soluble in KOHAq; soluble in HClAq or HBrAq with separation of Au; unacted on by other acids; decomposed at c. 250° to Au and O. Solutions of Au_2O in water give a marked absorption-spectrum (Krüss, *l.c.*). Raschig (*A.* 235, 341) describes bodies produced by reactions between aurous oxide and ammonia, and the same oxide and methylamine; when conc. NH_3Aq is added to Au_2O suspended in water, a black explosive compound, $NAu_3.NH_3$, is obtained, and when this is boiled with water or dilute acids *triauramine*, NAu_3, is produced; NH_2Me forms $NMeAu_2$.

Auro-auric oxide AuO (or $Au_2O.Au_2O_3$). According to Krüss (*B.* 19, 2544) this oxide is best obtained by heating AuO_3H_3 (*v. infra*) to 160°. AuO is described as a dark olive-brown powder; very hygroscopic, and must be kept over P_2O_5 (Krüss; *v.* also Schottländer, *A.* 217, 312). Conc. NH_3Aq acting on AuO is said to form the very explosive body *sesquihydraurylamine* $NH_3.N(AuOH)_3$ (Raschig, *A.* 235, 341).

Auric oxide Au_2O_3. $AuCl_3Aq$ is obtained by decomposing 1 pt. AuCl with 50 pts. water and filtering; the liquid is heated to boiling and *magnesia alba* (not *usta*) is added until the red colour of the liquid disappears; the pp. of AuO_3H_3 is filtered off, suspended in 20 pts. water, and kept in contact with 10 pts. HNO_3Aq, S.G. 1·4, for 12 hours; the residue is then digested at 100° for 6 hours, with reversed condenser attached, with HNO_3Aq and water as before; the residue from this digestion is washed with hot water until every trace of HNO_3 is removed; the AuO_3H_3 is then dried and very carefully heated (? to under 100°; the directions given by Krüss are not clear). Au_2O_3 gives off O at c. 110°; at 160° AuO remains; at 250° Au remains. It is easily reduced to Au.

When moist Au_2O_3 is treated with excess of NH_3Aq, or when excess of NH_3Aq is added to $AuCl_3Aq$ and the pp. is suspended in boiling NH_3Aq, or in water containing a little KOH, and then allowed to dry, a yellowish-brown solid, with a tinge of purple, is obtained, which explodes loudly when struck by a hammer or when heated to a little above 100°; the products of the decomposition are Au, NH_3, N, and H_2O. This substance is generally known as *fulminating gold*. Dumas (*A. Ch.* [2] 44, 167) gave to it the formula $(AuN.NH_3)_2.3H_2O$; this is confirmed by Raschig (*A.* 235, 341) for the body obtained by the action of NH_3Aq on Au_2O_3, but R. says that the product of the action of NH_3Aq on $AuCl_3Aq$ is a mixture of the preceding *auric diamine* with *auric imido-chloride*, NH.AuCl. Dilute H_2SO_4Aq with fulminating gold forms a very explosive body, $(AuN_2H_3)_4.H_2SO_4$ (R.).

Auric hydroxides. According to Krüss (*B.*

19, 2546) the normal hydroxide $Au_2O_3.3H_2O(=AuO_3H_3)$ is obtained by ppg. $AuCl_3Aq$ by *magnesia alba*, and removing the excess of magnesia by HNO_3Aq (for details *v. supra*, auric oxide); Krüss does not say at what temperature the pp. must be dried, nor does he give analyses. When this pp. is kept for some weeks over P_2O_5 the hydroxide $Au_2O_3.H_2O(=Au_2O_2.O_2H_2)$ is obtained (Krüss). Schottländer (*A.* 217, 312) failed to isolate AuO_3H_3; the highest percentage of water he obtained agreed with the formula $2Au_2O_3.3H_2O$, and the lowest with the formula $Au_2O_3.H_2O$. Schottländer (*l.c.*) by decomposing $AuSO_4$ (*v.* Sulphates) by water obtained the compound $3AuO.H_2O(=Au_3O_2.O_2H_2)$. These hydroxides, or hydrated oxides, yield Au when heated to c. 250° (*cf.* also Pelletier, *A. Ch.* [3] 15, 5, 113; Fremy, *A. Ch.* [3] 31, 478; Thomsen, *Th.* 3, 391).

Moist auric oxide (? AuO_3H_3) is a weak base; it dissolves in conc. H_2SO_4 and HNO_3Aq but the solutions are decomposed by water with ppn. of hydrated Au_2O_3. Schottländer (*A.* 217, 312) obtained $Au(NO_3)_3.HNO_3.3H_2O$ by dissolving the hydrated oxide in HNO_3Aq, S.G. 1·492, at 20°, heating to 100°, separating from ppd. Au, and crystallising by surrounding by a freezing mixture; by heating this acid nitrate to above 73° he obtained the normal nitrate $Au(NO_3)_3.xH_2O$. The same chemist obtained the sulphates $AuO.HSO_4$ and $AuSO_4$ from the nitrate. Hydrated auric oxide dissolves in alkalis, and from such solutions salts have been obtained known as *aurates*, *e.g.* $KAuO_2.3H_2O$. These salts are very easily reduced to Au (*v.* Aurates, vol. i. p. 363). Thomsen (*Th.* 3, 411) gives the following thermal data: $[AuO^3H^3,4HClAq] = 22,970$; $[AuO^3H^3,4HBrAq] = 36,780$; $[AuO^3H^3,3HClAq] = 18,440$; $[AuO^3H^3,3HBrAq] = 29,080$; $[Au^2,O^3,H^2O] = -13,190$.

Gold phosphide Au_2P_3. A grey solid, S.G. 6·67, formed by gently heating Au in P vapour; decomposed by heat (Schrötter, *W. A. B.* 1849. 301).

Gold purple. A name given to *purple of Cassius*, which is probably a mixture of SnO_2 with finely divided Au (*v.* Tin, oxides of).

Gold, salts of. Few compounds have been isolated produced by replacing H of acids by Au; those which are known are very easily reduced, like all the compounds of Au. The *normal nitrate* and *sulphate* $Au(NO_3)_3$, and $AuSO_4$ have been isolated (*v. supra*); also some *basic nitrates* and *sulphates*, and a few double salts, *e.g. gold-ammonium sulphite* and *gold-ammonium thiosulphate* (*v.* Nitrates, Sulphates, &c.).

Gold selenide. The pp. obtained by adding H_2Se to solutions of Au is probably a selenide (Berzelius, *P.* 8, 178).

Gold selenocyanides *v.* p. 348.

Gold sulphides. Two sulphides, Au_2S and AuS, have been isolated; these sulphides form thio- salts by reacting with alkaline sulphides, but the salts have scarcely been examined. When H_2S is passed into $AuCl_3Aq$, kept at 100°, Au is ppd.; if local cooling takes place the pp. contains varying proportions of combined S, but no definite compound is produced (L. Hoffmann a. Krüss, *B.* 20, 2369).

Aurous sulphide Au_2S. Obtained by passing H_2S into a solution of $KAuCy_4$ and then adding HClAq. The $KAuCy_4$ was prepared by decolourising $AuCl_3Aq$ by KCy, concentrating at 100°, adding dilute HClAq, evaporating, and washing the pp. with hot water. The $KAuCy_4$ was dissolved in KCyAq; the liquid was saturated with H_2S, excess of HClAq was added, and the whole was heated to boiling. The grey pp. which formed was washed with HClAq, then with C_2H_6O, ether, and CS_2, in succession, and finally with ether (L. Hoffmann a. Krüss, *B.* 20, 2373). Au_2S is a brownish-black powder; when freshly ppd. it dissolves in water, but after drying it is insoluble in water, and not decomposed by boiling dilute HClAq or H_2SO_4Aq. Dissolved by BrAq, forming $AuBr_3$ and H_2SO_4; oxidised readily by *aqua regia*, &c. It is not acted on by KOHAq even at 100°; slowly dissolved by alkaline monosulphides, easily by alkaline polysulphides, with formation of thio- salts of Au. Au_2S is soluble in KCyAq, and is reppd. by HClAq. It is completely decomposed by heating to 240° (H. a. K.).

Auro-auric sulphide $AuS(=Au_2S.Au_2S_3)$ (L. Hoffmann a. Krüss, *B.* 20, 2704). Obtained by passing H_2S into *cold* $AuCl_3Aq$ until the liquid is colourless, washing the pp. repeatedly, by decantation, with water, then with absolute alcohol, dry ether, and CS_2, successively, and finally with ether, and drying at 120°-130° $(8AuCl_3Aq + 9H_2S + 4H_2O = 8AuS + 24HClAq + H_2SO_4Aq)$. AuS is a black powder; when finely divided it transmits reddish light. Heated to 140° SO_2 is evolved, and at 250°-270° all S is removed, without the intermediate production of Au_2S. AuS is insoluble in all acids except *aqua regia*; it is gradually oxidised by BrAq to $AuBr_3$ and H_2SO_4; it is dissolved by alkaline sulphides; acids ppt. AuS from these solutions. Conc. KOHAq has no action when cold, but on heating Au is ppd. and K aurate and thio-aurate go into solution.

H. a. K. (*l.c.*) have repeated the experiments of Berzelius, Oberkampf, Yorke, and others, but have failed to obtain any other sulphides of gold except Au_2S and AuS. (For references to the older memoirs, *v.* H. a. K., *l.c.*)

Sodium aurosulphide $NaAuS.4H_2O$. Monoclinic prisms; very easily decomposed in air; obtained by fusing together Au, Na_2S, or Na_2CO_3, and S, lixiviating with water in an atmosphere of N, and evaporating in the same atmosphere *in vacuo*.

Gold sulphocyanides *v.* p. 350.

Gold telluride. Probably obtained by ppg. $AuCl_3Aq$ by H_2Te (Berzelius, *P.* 8, 178).

M. M. P. M.

GOSSYPOSE is identical with Raffinose.

GRAMININ $6C_6H_{10}O_5aq$. [209°]. S.G. 1·522. $[\alpha]_D = -38·89°$. S. 22·8 at 10°. A carbohydrate found in the roots of *Trisetum alpestre* and other plants (Ekstrand a. Johanson, *B.* 21, 597).

GRANATINE. An alkaloid in the bark of the root of the pomegranate (Durand, *J. Ph.* [4] 28, 168).

GRANDIFLORINE. Mol. w. 236·4. Obtained from the fruit of *Solanum grandiflorum* by extracting with water and alcohol. White powder giving the usual alkaloid reactions. Conc. H_2SO_4 and a little MnO_2 give a yellow colouration, turning green and then violet (Domingos Freire, *C. R.* 105, 1074).

GRANULOSE *v.* STARCH.

GRAPHITE, a form of carbon; *v.* vol. i. pp. 685-687.

GRAPHITIC ACID $C_{11}H_4O_5$. Formed in small quantity in the electrolysis of mineral acids and salts when the positive pole is pure graphite (Bartoli a. Papasogli, *G.* 12, 114 ; 13, 37).

Preparation.—Graphite, purified by boiling with acids and fusion with caustic potash, is intimately mixed with $KClO_3$ (3 pts.); the strongest nitric acid is added in sufficient quantity to render the mixture fluid; and the whole is either exposed to sunshine or heated to 60° for 3 or 4 days. When no more yellow vapours are evolved, the mixture is shaken into a large quantity of water, and the undissolved portion washed by decantation, dried at 100°, and treated with $KClO_3$ and HNO_3 as before. This process is repeated three or four times, the residue being graphitic acid (Brodie, *A.* 114, 6).

Properties.—Thin transparent yellow crystals; sl. sol. pure water, insol. water containing acids or salts. When heated it explodes with incandescence, giving off gas and leaving a black residue. When suspended in petroleum (boiling at 270°) and heated, water comes over between 100° and 200°, CO_2 being also evolved; the petroleum acquires a deep-red colour, and a black carbonaceous residue ($C_{22}H_2O_4$?) is left. When a solution of ammonium or potassium sulphide is poured upon graphitic acid it decomposes with decrepitation, forming a graphitoidal substance with metallic lustre. Acid solutions of cuprous and of stannous chloride behave in like manner. Gottschalk (*Z.* 1865, 652) represents graphitic acid by the formula $C_{11}H_4O_6$.

Salts.—When graphitic acid is shaken with aqueous ammonia it is transformed into a transparent jelly, without dissolving; after adding acids and drying *in vacuo* the residue has the same weight as the original graphitic acid. Moist graphitic acid shaken up with baryta-water, washed, and dried at 100° yields a compound containing 21·1 p.c. Ba ; after being suspended in water and decomposed by a stream of CO_2, the salt, dried at 100°, contains 13·3 p.c. Ba. This may be $Ba(C_{11}H_3O_5)_2$. It is hygroscopic and detonates when heated.

Nitro-graphitoic acid $C_{22}H_{17}NO_{13}$. An amorphous brown substance got by treating graphite from iron (Spiegeleisen) with HNO_3 (Schützenberger a. Bourgeois, *B* 8, 547). Sol. water, nitric acid, alkalis, and alcohol, insol. solutions of salts.

GRAPHON, a name given by Brodie to a supposed form of carbon of which graphitic acid was a compound (*v.* vol. i. p. 687).

GRATIOLIN $C_{20}H_{34}O_7$. A glucoside occurring in *Gratiola officinalis* (Marchand, *J. Chim. Méd.* 1845, 357; Walz, *Jahrb. pr. Pharm.* 21, 1). Amorphous substance, insol. ether, sl. sol. water, v. sol. alcohol. Conc. H_2SO_4 forms a purple solution, the colour being destroyed by water. Its aqueous solution is ppd. by tannin. Boiling dilute H_2SO_4 splits it up into a sugar, **gratioletin** $C_{17}H_{28}O_5$ a crystallisable substance insol. water and ether, and **gratioleretin** $C_{17}H_{28}O_3$ a resin, insol. water, sol. ether.

Gratiosolin $C_{46}H_{84}O_{25}$. Another glucoside occurring in *Gratiola officinalis*. Easily resolved by acids, alkalis, and even PbO into glucose and **gratiosoletin** $C_{40}H_{68}O_{17}$, a substance soluble in water and ppd. by tannin. Gratiosoletin is further resolved by boiling with dilute acids into glucose and a resinous mixture of gratiosoleretin $C_{34}H_{52}O_9$, sol. ether, and **gratiosoleretin hydrate** $C_{34}H_{56}O_{11}$, insol. ether. It need hardly be observed that all these formulæ are extremely doubtful.

GRAVITY, SPECIFIC, synonymous with *relative density*, *v.* p. 371.

GREVILLEA GUM. Occurs on the bark of *Grevillea robusta*. Yellowish-red, slightly translucent mass; swells up in water, forming a white emulsion, whence alcohol ppts. the gum, leaving 6 p.c. of a red resin in solution. If soaked in water containing a little KOH, lime, or K_2CO_3, the resulting solution gelatinises on addition of $FeCl_3$. The aqueous solution is lævorotatory, gives no pp. with lead acetate, but a blue gelatinous pp. with $CuSO_4$. It does not reduce Fehling's solution. It is oxidised by HNO_3 to mucic and a little oxalic acid. Boiling dilute H_2SO_4 forms a sugar (G. Fleury, *J. Ph.* [5] 9, 479).

GUAIACENE C_5H_8O. (118°). Obtained by distilling gum guaiacum. Identical with TIGLIC ALDEHYDE (*q. v.*).

GUAIACOL *v.* *Methyl derivative* of PYROCATECHIN.

GUAIACUM. *Resina guajaci sativa.* A resin which exudes from the stem of *Guajacum officinale*, a tree growing in the West Indies. It is composed of yellowish-brown lumps usually covered by a greenish-grey powder which renders it opaque. It is brittle. S.G. 1·205 to 1·226. When heated it emits an odour somewhat like that of gum benzoïn. Alcohol dissolves about 90 p.c. of the resin, the solution being ppd. by water. Ether and oil of turpentine dissolve much of it. It is nearly insol. water. It dissolves in alkalis. H_2SO_4 dissolves it, forming a splendid red solution, which yields a violet pp. with water; alcohol first colours the liquid violet-blue, and in larger quantity imparts to it a dirty bluish-green tint (Schiff, *A.* 111, 372). Both the powdered resin and its alcoholic solution turn green when exposed to the air and light (especially violet rays). The alcoholic solution is coloured blue by nitrous fumes, by CrO_3, by ozone, by chlorine, by K_3FeCy_6, by $AuCl_3$, by $KMnO_4$, by MoO_3, and by $FeCl_3$; the blue colour is removed by SO_2. Guaiacum tincture is coloured blue by concentrated, but not by dilute, cupric sulphate solution. Even dilute $CuSO_4$, in presence of HCy or of organic nitriles, also colour tincture of guaiacum blue (Schönbein, *Fr.* 8, 67; Schaer, *Fr.* 9, 430). According to Schönn (*Fr.* 9, 210) guaiacum tincture is coloured blue by a dilute solution of $CuSO_4$ in presence of NH_4Cl, $BaCl_2$, NH_4Br, KI, KCy, and NH_4F. Schönn also observes that guaiacum resin is coloured blue by solid lead acetate, by solid $CaCl_2$, by solid $BaCO_3$ on addition of a little HClAq, by $MnCl_2$, by mercurous nitrate, by a conc. solution of sodium sulphocyanide, and by cupric chloride even in very dilute solutions. Arterial blood colours tincture of guaiacum blue. According to Schönbein (*J. pr.* 102, 164) exposure to light deprives tincture of guaiacum of the power of being turned blue by ozone. Heat also deprives the resin of this property (Hager, *Fr.* 26, 261). Potash-fusion forms protocatechuic acid from guaiacum. Dry distillation forms tiglic aldehyde C_5H_8O (118°), guaiacol $C_6H_4(OH)(OMe)$ (200°), creosol $C_6H_3Me(OH)(OMe)$, and pyroguaiacin $C_{18}H_{18}O_3$ [181°] (Hlasiwetz, *A.* 106, 361). Distillation with zinc-dust forms creosol, toluene, *m*- and *p*-xylene, ψ-cumene, and guaiene $C_{12}H_{12}$ (Bötsch, *M.* 1, 615). Alkalis extract guaiaretic acid from guaiacum (Unverdorben, *P.* 16, 369). According to Hadelich (*J. pr.* 87, 321) guaiacum also contains guaiaconic acid (sol. ether), and a resin $C_{14}H_{14}O_4$ or $C_{20}H_{20}O_6$ (insol. ether) [200°], sol. alkalis and reppd. by acids.

Guaiaretic acid $C_{20}H_{26}O_4$. [75°-80°]. Powdered guaiacum is boiled with milk of lime for half an hour, and the dried insoluble residue exhausted with hot alcohol; the alcoholic solution is evaporated and the residue dissolved in warm aqueous NaOH (S.G. 1·3). On cooling, sodium guaiaretate separates, and may be purified by recrystallisation. The free acid is then got by adding HClAq (Hlasiwetz a. Gilm, *A.* 119, 266; *cf.* Thierry, *J. Ph.* 27, 381; Hlasiwetz, *A.* 112, 182).

Properties.—Brittle, concentrically grouped needles (from HOAc). Colourless; permanent in the air. Sol. alcohol, ether, hot HOAc, and CS_2. Sol. KOHAq; insol. NH_3Aq. Ppd. by adding NH_4Cl to its solution in KOHAq. Ppd. as a resin by adding water to its alcoholic solution. Its alcoholic solution is lævorotatory, and is coloured grass-green by $FeCl_3$. Chlorine-water does not colour the alcoholic solution either green or blue. The aqueous solution is not coloured blue by fuming HNO_3. When slowly distilled it yields guaiacol and pyroguaiacin $C_{19}H_{22}O_3$. [183°]. Potash fusion gives protocatechuic acid. When bromine is dropped into a solution of guaiaretic acid in CS_2 there is formed $C_{20}H_{22}Br_4O_4$ which crystallises from alcohol in needles.

Salts.—The guaiaretates of the alkalis are crystallisable; those of the alkaline earths are amorphous pps. The neutral salts are stable only in presence of alkali; when boiled with water they are converted into acid salts.—K_2A'' 2aq: scales (from alcohol).—K_2A'' 3aq.—HKA''aq: obtained by boiling the preceding salt with dilute alcohol; crystalline pp.—Na_2A'' 2aq: shining laminæ.—$NaHA''$aq: laminæ.—$BaA''x$aq.—$Pb_2C_{20}H_{22}O_4$: amorphous pp.

Guaiaconic acid $C_{19}H_{20}O_5$ (?). [95°-100°]. Remains in the mother liquor from which sodium guaiaretate (*v. supra*) has crystallised (Hadelich, *J. pr.* 87, 321). The solution is evaporated, the residue extracted with alcohol, and the alcoholic solution treated with CO_2. Amorphous. V. sol. alcohol, ether, chloroform, and HOAc. Lævorotatory. When heated with HClAq at 180° it forms MeCl and pyrocatechin (Herzig, *M.* 3, 125, 823). Nitrous acid gas passed into its ethereal solution forms di-nitro-guaiacol. The K and Na salts are sol. water and alcohol; the Ba and Pb salts are insoluble.

GUAIENE $C_{12}H_{12}$. [98°]. Obtained by distilling resin of guaiacum or pyroguaiacin with zinc-dust (Bötsch, *M.* 1, 618; Wieser, *M.* 1, 602). Laminæ (by sublimation) with blue fluorescence. Volatile with steam. Sol. alcohol and ether. Conc. H_2SO_4 forms a green solution; on adding water the hydrocarbon is not reppd. CrO_3 in HOAc forms guaiene-quinone $C_{12}H_{10}O_2$ which by sublimation forms lemon-yellow needles, [122°], m. sol. water, insol. $NaHSO_3$Aq. Guaiene forms with picric acid a compound crystallising in slender needles, [123°], v. sl. sol. alcohol.

GUAIOL *v.* Tiglic aldehyde.

GUANAMINE. The substance to which this name was given by Nencki, was subsequently called by him Formoguanamine (*q. v.*).

DIGUANIDE $C_2H_7N_5$ *i.e.* $\begin{matrix}NH{:}C(NH_2)\\ NH{:}C(NH_2)\end{matrix}\!>\!NH$. *Biguanide. Guanidyl-guanidine.*

Formation.—1. By heating a salt of guanidine with cyanamide; the yield being small (Rathke, *B.* 12, 776).—2. By the action of PCl_5 or bromine on a mixture of thio-urea and guanidine sulphocyanide; the yield is very small.—3. By heating di-cyan-di-amide with an ammoniacal solution of $Cu(OH)_2$ at 110°; the resulting copper derivative being decomposed by H_2S (Herth, *M.* 1, 88).

Preparation.—An alcoholic solution of dicyandiamide is heated with ammonium chloride in a sealed tube for 8 hours at 105° (Smolka a. Friedreich, *M.* 9, 228).

Properties.—The free base, liberated from its sulphate by baryta, is amorphous and alkaline in reaction. It expels ammonia from its salts. Boiling diluted H_2SO_4 splits it up into NH_3 and CO_2.

Salts.—$B''H_2SO_4$aq: crystals, v. sol. water. —$B''_2H_2SO_4$aq: from the sulphate of the copper derivative and H_2S (Emich, *M.* 4, 409); large colourless crystals, with neutral reaction, v. sol. water.—The **hydrochloride** and **nitrate** crystallise in soluble needles.—$B''H_2PtCl_6$ 2aq: soluble crystals. — **Copper derivative** $(C_2H_6N_5)_2Cu$ 2aq. Obtained by heating an ammoniacal solution of cupric oxide with di-cyan-di-amide (Herth, *M.* 1, 88). Large flat prisms of brick-red colour; v. sl. sol. cold, sol. hot, water, forming a deep-violet solution, turned blue by acids. Alkaline in reaction. — $(C_2H_6N_5)_2CuH_2SO_4$ 3aq: slender red needles, sl. sol. water. Formed by adding ammoniacal $CuSO_4$ to a solution of a salt of diguanide.

References.—Iso-butyl, ethyl-, methyl-, and Phenyl diguanide.

GUANIDINE CH_5N_3 *i.e.* $HN{:}C(NH_2)_2$. Mol. w. 59.

Formation.—1. Together with parabanic acid, and small quantities of xanthine, oxaluric acid, and urea, by the action of HCl (S.G. 1·10) and $KClO_3$ (12 g.) on guanine (20 g.) in the cold (Strecker, *A.* 118, 151).—2. By heating biuret to 165° in dry gaseous HCl (Finckh, *A.* 124, 335).—3. By heating chloro-picrin for several hours at 100° with a strong alcoholic solution of ammonia (Hofmann, *Z.* [2] 2, 1073; 4, 721; *B.* 1, 145; *A.* 139, 107).—4. In small quantity by the action of aqueous ammonia at 150° on ortho-carbonic ether (Hofmann, *A.* 139, 111).—5. Together with urea by the action of dry ammonia on carbonyl chloride $COCl_2$ (Bouchardat, *C. R.* 69, 961; Fenton, *C. J.* 35, 793).—6. By heating cyanamide in alcoholic solution with ammonium chloride at 100° (Erlenmeyer, *Z.* [2] 7, 28; *A.* 146, 259).—7. By heating cyanogen iodide with alcoholic NH_3 for 8 hours at 100° (Bannow, *B.* 4, 161). According to Ossikovsky (*Bl.* [2] 18, 161) other products, including a volatile fatty acid, are formed at the same time. 8. Together with urea, ammelide, and biuret, by the electrolysis of a solution of ammonia with carbon electrodes (Millot, *Bl.* [2] 46, 244). 9. Among the products of the oxidation of egg-albumen by $KMnO_4$ in presence of magnesia (Lossen, *A.* 201, 369).

Preparation.—Dry ammonium sulphocyanide is heated for 20 hours at 180°–190°. The residue consists mainly of guanidine sulphocyanide, no gaseous product being given off. The guanidine sulphocyanide is purified by recrystallisation from water or alcohol, and is converted into the carbonate by mixing a solution of it (100 g.) with a solution of K_2CO_3 (58 g.), evaporating, and dissolving out the potassium sulphocyanide with alcohol. The guanidine carbonate is then recrystallised from water, and the base liberated by dissolving in the calculated quantity of dilute H_2SO_4 and adding the calculated quantity of baryta (Delitsch, *J. pr.* 2] 8, 240; 9, 1; Volhard, *J. pr.* [2] 9, 10).

Properties.—Crystalline, strongly alkaline mass, having a caustic taste. When exposed to the air it deliquesces and absorbs carbonic acid.

Reactions.—1. When boiled with *baryta water* it gives ammonia and urea; the urea subsequently breaking up into CO_2 and ammonia (Baumann, *B.* 6, 1376). Hence boiling concentrated acids and alkalis give only CO_2 and NH_3 (Ossikowsky, *B.* 5, 668).—2. With *hypobromite* or *hypochlorite of sodium*, two-thirds of the nitrogen is evolved, one-third remaining behind, probably as cyanate (Fenton, *C. J.* 35, 14).—3. *Benzoic anhydride* acting at 100° on guanidine carbonate forms *s*-di-benzoyl-urea [210°] (McCreath, *B.* 7, 1739).—4. With *chloro-formic* (chloro-carbonic) *ether* it forms guanidine dicarboxylic ether $HN.C(NH.CO_2Et)_2$. This ether is converted by alcoholic ammonia at 100° into guanidine mono-carboxylic ether (so-called guanoline): $HN:C(NH_2)NH.CO_2Et$ (M. Nencki, *J. pr.* [2] 17, 237).—5. When the salts of guanidine with *fatty acids* are heated there are formed 'guanamines.' Thus guanidine formate forms formo-guanamine $C_3H_5N_5$ while guanidine acetate gives acetoguanamine $C_4H_7N_5$ (*v. infra*).—6. Salts of guanidine heated with cyanamide form diguanide (*v. supra*).—7. When fused with *urea*, guanidine carbonate forms guanyl-urea $C_2H_6N_4O$. 8. An aqueous solution of guanidine carbonate (2 mols.) boiled with an alcoholic solution of *phenanthraquinone* forms small colourless prisms of the base $C_{16}H_{14}N_6$ probably

$$\begin{array}{l} C_6H_4.C:N.C(NH_2):NH \\ |\qquad | \\ C_6H_4.C:N.C(NH_2):NH \end{array}$$

. It is alkaline in reaction, absorbs CO_2 from the air, and forms a crystalline hydrochloride $B''H_2Cl_2$ (Wense, *B.* 19, 761).—9. In like manner *benzil* (1 mol.) boiled with guanidine carbonate (2 mols.) in dilute alcoholic solution forms benzil-di-guanidide $C_{16}H_{16}N_6$ which may probably be written $HN:C(NH_2).N:CPh.CPh:N.C(NH_2):NH$. It forms granular crystals, reacts alkaline, absorbs CO_2 from the air, and gives a hydrochloride crystallising in long needles, and a platinochloride $B''H_2PtCl_6$ crystallising in plates (Wense, *B.* 19, 763).—10. When *benzil* (1 mol.) is boiled with a smaller quantity of guanidine carbonate (1 mol.) in aqueous-alcoholic solution, there is formed benzil mono-guanidide $C_{15}H_{13}N_3O$ probably $O:CPh.CPh:N.C(NH_2):NH$. This body forms white oblong plates, sol. alcohol, insol. water. It is alkaline in reaction (Wense, *B.* 19, 762).—11. *Aceto-acetic acid* digested in alcoholic solution with guanidine carbonate for a few hours forms 'methyl-guanacil' $C_5H_7N_3O$ *i.e.*

$HN:C\left<\begin{matrix}NH.CMe\\NH.CO\end{matrix}\right>CH$. This body crystallises from water in prismatic needles; sol. hot, sl. sol. cold, water, v. sl. sol. alcohol (Behrend, *B.* 19, 219).—12. *Phenyl-thio-carbimide* (3 pts.) heated with alcohol and guanidine carbonate (2 pts.) at 100° forms the crystalline compound $NHPh.CS.NH.C(NH_2):NH$ [176°] (Bamberger, *B.* 13, 1581; 14, 2638).

Salts.—$B'HCl$: regular needles; v. sol. alcohol. – $B'_2H_2PtCl_6$: yellow needles or prisms, v. sol. water, v. sl. sol. alcohol.—$B'HClHg_2Cl_4$.—$B'HAuCl_4$: long needles.—$B'HBr_3$: from guanidine carbonate (1 mol.) and bromine (3 mols.). Large red prisms which easily lose bromine (Kamenski, *B.* 11, 619).—$B'HI_3$: prisms.—$B'HNO_3$: ppd. as a crystalline powder by adding KNO_3 to a solution of the hydrochloride. Formed also by rubbing guanidine sulphocyanide with pure HNO_3 and filtering before deflagration ensues (Jousselin, *C. R.* 88, 1086). Laminæ (from hot water); sl. sol. cold water. Mixed with silver nitrate it gives the crystalline compound $B'AgNO_3$.—**Sulphate** crystallises in the regular system and is v. e. sol. water.—$B'_2H_2CO_3$. May be obtained by boiling the sulphocyanide with diluted H_2SO_4, filtering, treating with $BaCO_3$, and allowing the liquid to evaporate spontaneously (Jousselin). Dimetric octahedra or prisms; v. sol. water, insol. alcohol. Permanent in the air. When heated above 120° it gives off water, CO_2 and NH_3, and leaves a yellow residue resembling mellon.—**Oxalate** $B'H_2C_2O_4aq$: colourless crystals, sl. sol. water.—**Lactate** forms regular crystals.—**Cyanurate** $B'C_3N_3O_3H_3$: silky needles (Bamberger, *B.* 20, 68).—**Sulphocyanide** $B'HSCy$. [120°]. S. 73 at 0°; 135 at 15° (Engel, *Bl.* [2] 44, 424). Formed as above. Large flexible laminæ with fatty lustre (from water or alcohol). Not deliquescent. At 150° it gives off NH_3 and leaves melam. Upon this salt mercuric oxide has no action in alcoholic solution, but in aqueous solution it gives a pp. composed thus: $B'.HSCN,Hg(SCN)_2HgO$. The reaction taking place as follows: $3B'HSCN + 2HgO + 3H_2O = B'HSCN, Hg(SCN)_2,HgO + 6NH_3 + 2CO_2$. The pp. is converted by acetic acid into a mixed acetate and sulphocyanide of mercury. The same pp. is converted by concentrated HCl into crystalline plates of $CN_3H_5,HCl2HgCl_2$ (Byk, *J. pr.* [2] 20, 330). Fused guanidine sulpho-cyanide treated with finely divided lead (got by reducing the oxide by hydrogen) is partially converted into '**cyano-melamidine**,' $C_7H_{13}N_{15}O$, a body which is soluble in water but is separated from the original salt by its insolubility in alcohol. Cyanomelamidine forms salts of melamine when treated with HCl, $FeCl_3$ or H_2SO_4. With HNO_3

it forms the nitrate of ammeline. With $KMnO_4$ it gives melamine (Byk, *J. pr.* [2] 20, 338).

Nitroso-guanidine CH_4N_4O *i.e.* $NO.N.C(NH_2)_2$. Formed by passing nitrous acid gas through dry guanidine nitrate suspended in conc. HNO_3. The salt slowly dissolves, and on adding water to the solution, nitroso-guanidine is ppd. in slender needles, which are recrystallised from boiling water (Jousselin, *C. R.* 88, 814). Needles; sl. sol. cold water and alcohol, insol. ether. Boiling conc. KOHAq decomposes it, giving off NH_3. Warm conc. HNO_3 dissolves it, and on cooling the salt $B'HNO_3$ separates in large plates; this salt is efflorescent and decomposed by water. HClAq dissolves nitroso-guanidine yielding slender iridescent plates which are decomposed by water. On dissolving nitroso-guanidine in water, adding a drop of very dilute aqueous KOH and a drop of aqueous $FeSO_4$ a purple colour is produced. If alcohol and ether are added to the coloured solution minute dark-red crystals are deposited. Finely divided iron acting on nitroso-guanidine suspended in water at 40° also forms a purple colour, but after some time this disappears, NH_3 being evolved. The solution evaporated at 60° leaves an unstable sulphur-yellow residue which appears to be CH_4N_4O.

Acetoguanamine $C_4H_7N_5$ *i.e.* $\mathrm{CMe}\Big<\begin{matrix}\mathrm{N-C(NH)}\\ \mathrm{NH.C(NH)}\end{matrix}\Big>\mathrm{NH}$ (Weith, *B.* 9, 458), or $\mathrm{CMe}\Big<\begin{matrix}\mathrm{N.C(NH_2)}\\ \mathrm{N{:}C(NH_2)}\end{matrix}\Big>\mathrm{N}$ (Claus, *B.* 9, 722). *Ethenyl-diguanide. Di-amido-methyl-triazoline.* [265°]. Formed by heating dry guanidine acetate for 15 minutes at 230°; the resulting acetoguanamine acetate being extracted by water and decomposed by NaOHAq (Nencki, *B.* 7, 776, 1585). Trimetric laminæ; sl. sol. cold, v. sol. hot, water. V. sol. alcohol. Slightly alkaline in reaction. Chlorine passed into acetoguanamine suspended in water forms a granular pp. $C_4H_5Cl_2N_5$ (Nencki, *B.* 9, 237). This is insol. water, sol. alkalis; by heating with dilute HCl it is converted into an isomeric body which crystallises from dilute acetic acid in needles, is insol. alkalis and forms the salts $(C_4H_5Cl_2N_5)_2H_2PtCl_6$ and $C_4H_5Cl_2N_5AgNO_3$.

Salts.—B'HCl 2aq: tables or prisms.—$B'_2H_2PtCl_6$: yellow crystalline pp.; v. sol. water.—$B'HNO_3$: prisms, v. sol. water.—$B'_2H_2SO_4$ 2aq: plates, v. e. sol. water.—B'_2AgNO_3: small plates (from hot water).

Acetoguanide $C_4H_6N_4O$ *i.e.* $\mathrm{CMe}\Big<\begin{matrix}\mathrm{N.C(NH)}\\ \mathrm{NH.CO}\end{matrix}\Big>\mathrm{NH}$ or $\mathrm{CMe}\Big<\begin{matrix}\mathrm{N.C(OH)}\\ \mathrm{N{:}C(NH_2)}\end{matrix}\Big>\mathrm{N}$. *Oxy-amido-methyl-triazoline.* Formed by boiling acetoguanamine (1 pt.) with KOH (2 pts.) and water (4 pts.) for 1½ hours, and ppg. with HOAc (Nencki, *B.* 9, 233). Crystalline pp. Almost insol. water, alcohol, dilute HOAc, and aqueous NH_3, v. sol. alkalis and HClAq.—$C_4H_5NaN_4O$ 2aq.—$C_4H_5KN_4O$ 2aq.—$C_4H_6N_4OHCl$: needles.—$C_4H_6N_4OAgNO_3$.

Acetoguanamide $C_4H_5N_3O_2$ *i.e.* $\mathrm{CMe}\Big<\begin{matrix}\mathrm{N-CO}\\ \mathrm{NH.CO}\end{matrix}\Big>\mathrm{NH}$ or $\mathrm{CMe}\Big<\begin{matrix}\mathrm{N.C(OH)}\\ \mathrm{N{:}C(OH)}\end{matrix}\Big>\mathrm{N}$. *Di-oxy-methyl-triazoline.* From acetoguanamine (1 pt.), by warming with conc. H_2SO_4 (2 pts.) at 150°. Small needles (from alcohol); v. e. sol. water, acids, and alkalis, sl. sol. alcohol. On warming with nitric acid (S.G. 1·3) it yields cyanuric acid. Chlorine passed into its aqueous solution forms crystalline $C_4H_5Cl_2N_3O_2$. Sl. sol. hot water, being decomposed thereby with formation of cyanuric acid.—B'HCl: needles.—$B'_2H_2PtCl_6$ 4aq.

References.—BROMO-, CHLORO-, OXY-, BENZYL-, ETHYL-, METHYL-, NAPHTHYL-, NITRO-PHENYL-, PHENYL-, TOLYL-, and XYLYL- GUANIDINES.

GUANIDINE CARBOXYLIC ETHER $C_4H_9N_3O_2$ *i.e.* $HN{:}C(NH_2).NH.CO_2Et$. *Guaniline.* [115°]. Formed as below. Trimetric laminæ (from water or alcohol); the crystals contain aq and melt at 100°; when anhydrous it melts at 115°.—$B'HNO_3$: trimetric prisms.—$B'_2H_2SO_4$.—$B'_2H_2PtCl_6$.

Guanidine dicarboxylic ether $C_7H_{13}N_3O_4$ *i.e.* $NH{:}C(NH.CO_2Et)_2$. [162°]. Formed by slowly adding $ClCO_2Et$ to a concentrated alcoholic solution of guanidine (Nencki, *J. pr.* [2] 17, 237). Needles; insol. water, v. sol. alcohol and ether. Alcoholic NH_3 converts it at 100° into guanidine carboxylic ether.

GUANIDO-ACETIC ACID $C_3H_7N_3O_2$ *i.e.* $NH{:}C(NH_2).NH.CH_2.CO_2H$. *Glycocyamine.* Formed by allowing an aqueous solution of glycocoll, cyanamide, and a little NH_3 to stand for some days (Strecker, *C. R.* 52, 1212). Formed also by heating glycocoll with guanidine carbonate (Nencki a. Sieber, *J. pr.* [2] 17, 477). Crystals, sl. sol. water, insol. alcohol.—$B'_2H_2PtCl_6$ 3aq.—$(C_3H_6N_3O_2)Cu$: blue pp.—B'HCl: prisms.

By heating to 160° it is split up into water and the hydrochloride of 'glycocyamidine' $C_3H_5N_3O$ or $\mathrm{NH{:}C}\Big<\begin{matrix}\mathrm{NH.CO}\\ \mathrm{NH.CH_2}\end{matrix}\Big>$, a base which crystallises in laminæ, v. sol. water, and forms the salts $C_3H_5N_3OHCl$ and $(C_3H_5N_3O)_2H_2PtCl_6$ 2aq.

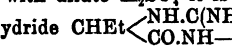
GUANIDO-BENZENE *p*-SULPHONIC ACID $C_7H_9N_3SO_3$ *i.e.* $SO_3H.C_6H_4.NH.C(NH_2){:}NH$. Formed by heating amido-benzene *p*-sulphonic acid (10 g.) with cyanamide (3 g.), water (200 c.c.), and ammonia (23 drops) at 100° for three days (Ville, *C. R.* 104, 1281). Brilliant needles, v. sl. sol. cold water, insol. alcohol and ether. Neutral to litmus. Decomposes at 180°. Dissolves without alteration in H_2SO_4 and HClAq. NaOBr gives a purple colouration, with evolution of nitrogen.

GUANIDO-BENZOIC ACID $C_8H_9N_3O_2$ *i.e.* $NH{:}C(NH_2).NH.C_6H_4.CO_2H$. *Benzglycocyamine.* Formed by allowing an alcoholic solution of *m*-amido-benzoic acid and cyanamide to stand, after addition of a little ammonia (Griess, *B.* 7, 575). Formed also by boiling the dicyanide of *m*-amido-benzoic acid with caustic potash (Griess, *B.* 3, 703), and by treating the compound $NH{:}C(OEt).NH.C_6H_4.CO_2H$ with conc. NH_3Aq (Griess, *B.* 8, 323). Thin four-sided plates (containing aq); m. sol. hot water. Boiling baryta-water gives uramido-benzoic acid, *m*-amido-benzoic acid, urea, and NH_3.—$B'_2H_2PtCl_6$.—B'HCl.

Reference.—Vol. i. p. 462.

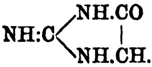
Guanido-di-benzoic acid *v.* vol. i. p. 157.

GUANIDO-BUTYRIC ACID $C_5H_{11}N_3O_2$ *i.e.* $NH{:}C(NH_2).NH.CHEt.CO_2H$. *Oxybutyrocyamine. Amidobutyro-cyamine.* Formed by adding cyanamide and a few drops of NH_3Aq to a cold saturated solution of α-amido-butyric acid.

Crystals are deposited in about a month, and are purified by recrystallisation from water containing a little NH_3 (Duvillier, *C. R.* 91, 171). Long slender needles, sl. sol. cold water, v. sol. dilute acids, almost insol. alcohol and ether. By boiling with dilute H_2SO_4 it is converted into the anhydride 
$CHEt\left\langle\begin{array}{l}NH.C(NH)\\CO.NH\text{——}\end{array}\right\rangle$, which crystallises from water in long transparent needles (containing aq); sol. alcohol.

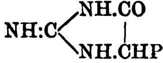
GUANIDO-ETHANE SULPHONIC ACID $NH:C(NH_2).NH.CH_2.CH_2.SO_3H$. *Tauro-cyamine.* [226°]. Prepared by heating taurine (1·578 grm.) with cyanamide (·85 grm.), and enough water to dissolve them, for five hours at 120°. Evaporated to crystallisation. The yield is 1·6 grms. (Dittrich, *J. pr.* [2] 18, 76). Hexagonal prisms. Readily sol. water. Insol. alcohol and ether. No salts have been obtained.

GUANIDO-HEXOIC ACID $C_7H_{15}N_3O_2$ *i.e.* $NH:C(NH_2).NH.CH(CH_2Pr).CO_2H$. *Amido-caprocyamine.* Formed by mixing an aqueous solution of leucine with cyanamide and a few drops of NH_3Aq, and allowing the liquid to stand for some time (Duvillier, *C. R.* 104, 1290). Radiating plates; sl. sol. cold, m. sol. hot, water, sl. sol. alcohol. When boiled with dilute H_2SO_4 for several hours it changes to the anhydride


$NH:C\left\langle\begin{array}{l}NH.CO\\ \qquad\ |\\NH.CH.C_4H_9\end{array}\right.$, which crystallises in groups of needles; S. (alcohol) 17 at 22°; sl. sol. cold, m. sol. hot, water. This anhydride ('amido-caprocyamidine') readily takes up water, reproducing guanido-hexoic acid.

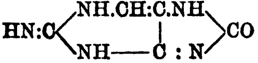
α-GUANIDO-PROPIONIC ACID *v.* ALACREATINE.

β-Guanido-propionic acid $C_4H_9N_3O_2$ *i.e.* $NH:C(NH_2).NH.CH_2.CH_2.CO_2H$. Formed by adding a little NH_3Aq to a solution of β-amido-propionic acid (20 pts.) and cyanamide (7 pts.) (Mulder, *B.* 8, 1261; 9, 1902). Crystals; not decomposed below 200°.—B'HCl: very deliquescent needles.

α-GUANIDO-VALERIC ACID $C_6H_{13}N_3O_2$ *i.e.* $NH:C(NH_2).NH.CHPr.CO_2H$. '*Oxy-valero-cyamine.*' From α-amido-valeric acid, an aqueous solution of cyanamide, and a little NH_3 (Duvillier, *C. R.* 91, 171). Small cubic crystals, sl. sol. water, v. sl. sol. alcohol; insol. ether. Boiling dilute H_2SO_4 converts it into the anhydride $C_6H_{11}N_3O$ or 
$NH:C\left\langle\begin{array}{l}NH.CO\\ \qquad\ |\\NH.CHPr\end{array}\right.$, which forms delicate needles (containing ½aq); m. sol. water and alcohol.

GUANILINE *v.* GUANIDINE CARBOXYLIC ETHER.

GUANINE $C_5H_5N_5O$ *i.e.*


$HN:C\left\langle\begin{array}{l}NH.CH:C.NH\\ \qquad\qquad\ \ |\\NH\text{——}C:N\end{array}\right\rangle CO$ (Fischer, *B.* 15, 455).

Mol. w. 151. Occurs in all kinds of guano, especially in Peruvian guano (Unger, *A.* 51, 395; 59, 58). Constitutes the greater part of the excrement of the garden spider, and found in the green gland of the fresh-water crayfish, and in the Bojanian organ of the pond-mussel (Gorup-Besanez a. F. Will, *A.* 69, 117; Griffiths, *Pr.* 38, 187). Found in the pancreas of horses (Scherer, *A.* 112, 257) and oxen (Baginsky, *H.* 8, 396), in the scales of the bleak (Barreswil, *C. R.* 53, 246), and in the excrement of the heron (Hoppe-Seyler, *Med.-Chem. Unters.* 1871, 582). Guanine occurs as a concretion in the knee-joints of pigs suffering from guano-gout (Virchow, *Z.* 1866, 377), and perhaps also in the urine of such pigs (Pecile, *A.* 183, 141). It has also been found to the amount of 5 or 6 p.c. in the sperm of the salmon (Piccard, *B.* 7, 1714), and, together with other bases, in the extract obtained by boiling yeast with water (Schützenberger, *B.* 7, 192). Kossel (*H.* 8, 404) finds guanin in the liver, spleen, and embryonic muscle of oxen.

Preparation.—Guano suspended in water is gradually mixed with milk of lime; the liquid is heated to boiling, and the brown solution is strained through a cloth filter, this treatment being repeated till the liquid becomes colourless. Guanine and uric acid remain almost wholly undissolved, and this residue is now repeatedly boiled with carbonate of sodium, and the united solutions are mixed with acetate of sodium, and then with hydrochloric acid in sufficient quantity to produce a strong acid reaction. The pp., consisting of guanine and uric acid, is washed with moderately dilute hydrochloric acid, then boiled with the acid, and the solution of hydrochloride of guanine, filtered from the uric acid, is evaporated. The hydrochloride of guanine thus obtained still contains uric acid, to remove which the guanine is ppd. from the solution by boiling with dilute ammonia, then dissolved in hot nitric acid to decompose the uric acid; and from the nitrate of guanine, which crystallises from this solution, the pure base is ppd. by ammonia (Strecker, *A.* 118, 151). According to Neubauer and Kerner (*A.* 101, 318), pure guanine is most easily obtained by dissolving the compound of guanine with mercuric chloride in very dilute hydrochloric acid, decomposing the compound with H_2S, and ppg. the colourless filtrate with ammonia.

Properties.—White amorphous powder, insol. water, alcohol, and ether. It is sl. sol. conc. NH_3Aq, and is deposited as crystals by spontaneous evaporation of the ammoniacal solution (Drechsel, *J. pr.* [2] 24, 44). When guanine is evaporated with fuming HNO_3 a yellow residue is left, which is turned red by ammonia, and then becomes purple on warming (*cf.* Von Brücke, *M.* 7, 617). A solution of a salt of guanine gives an orange pp. with K_2CrO_4 and a brown pp. with K_3FeCy_6. A saturated solution of picric acid gives an orange-yellow pp. (Capranica, *H.* 4, 233).

Reactions.—1. *Nitrous acid* converts it into xanthine, imidogen being displaced by oxygen (Strecker, *A.* 108, 141).—2. $KClO_3$ and HCl form guanidine and parabanic acid, together with smaller quantities of oxaluric acid, xanthine, and urea.—3. $KMnO_4$ and NaOH at 80° form oxyguanine $C_{10}H_{14}N_8O_9$, which may be ppd. by acids as a jelly, insol. water, alcohol, and dilute HClAq, sol. alkalis (Kerner, *A.* 103, 251). With ammoniacal $AgNO_3$ oxyguanine gives a silver derivative.

Salts.—The compounds of guanine with acid are decomposed by water. Guanine does not appear to form an acetate or formate.—B'HCl aq: delicate needles, deposited from a solution of guanine in hot conc. HClAq. — B'HCl 2aq (Scherer, *A.* 112, 277). — $B'H_2Cl_2$: from guanine and gaseous HCl; gives off half its acid at 100° (Unger).—B'HBr aq : prismatic needles.—B'HI aq : prismatic needles, sl. sol. water, v. sol. HIAq. —$B'HClPtCl_4$ 2aq (?) : orange-yellow crystals (U.).—$B'_2H_2Cl_2HgCl_2$ aq : ppd. when alcoholic $HgCl_2$ is added to a strong solution of guanine hydrochloride.—$B'_2H_2Cl_2ZnCl_2$ 3aq : large crystals, obtained by adding guanine hydrochloride to a strong solution of $ZnCl_2$. — $B'_4H_4Cl_4Cd_5Cl_{10}$ 9aq. — $B'HNO_3$ 1½aq : hair-like interlacing needles, deposited from a solution of guanine in boiling HNO_3 as it cools.—$B'(HNO_3)_2$ 2aq : short prisms.—$B'_3(HNO_3)_4$ 4aq.—$B'_3(HNO_3)_5$ 5½aq.—$B'_2H_2SO_4$ 2aq : obtained by diluting with water a solution of guanine in conc. H_2SO_4. Long needles. — $B'_3(H_2C_2O_4)_2$: separates as crystals on mixing a solution of guanine hydrochloride with one of ammonium oxalate.—Tartrate $B'_3(H_6C_4O_6)_2$ 2aq : yellowish radiating nodules.

Metallic derivatives $C_5H_3Na_2N_5O$ 4aq : deposited on adding alcohol to a strong solution of NaOH saturated with guanine. Confused efflorescent laminæ, which rapidly absorb CO_2 from the air. Decomposed by water.—$C_5H_3BaN_5O$ (at 110°) : pointed prisms. Separates on cooling from a solution of guanine in baryta-water.— $B'HgCl_2$ 2½aq : obtained as a crystalline powder on adding cold saturated aqueous $HgCl_2$ to a solution of guanine hydrochloride. V. sol. acids and KCy aq.—$B'AgNO_3$: flocculent pp.; formed by mixing solutions of silver nitrate and guanine nitrate. Crystallises from hot HNO_3 in slender needles (Strecker).

Reference.—BROMO-GUANINE.

GUANOLINE *v.* GUANIDINE CARBOXYLIC ETHER.

GUANYL-PHENYL-THIO-UREA $C_8SN_4H_{10}$ *i.e.* NHPh.CS.NH.C(NH_2):NH. [176°]. Prepared by heating a mixture of phenyl-thiocarbimide (3 pts.), guanidine carbonate (2 pts.), and alcohol at 100° (Bamberger, *B.* 13, 1580; 14, 2638). Colourless monoclinic crystals. V. sol. alcohol. Alkaline in reaction. Slowly decomposed by boiling water into guanidine, phenyl thiocarbimide, aniline, H_2S, and CO_2. Boiling HClAq, forms guanidine, aniline, H_2S, and CO_2.

Salts.—B'HCl : long glistening needles, more soluble in alcohol than in water; on boiling with water it evolves H_2S; $CuSO_4$ produces a violet pp. turning black on heating.—$B'_2H_2SO_4{}^{\times}$: pearly plates.—$B'_2H_2C_2O_4{}^{\times}$: white glistening scales.—$B'C_6H_2(NO_2)_3OH$: yellow felted needles.

GUANYL-THIO-UREA $C_2H_6N_4S$ *i.e.* SC(NH_2).NH.C(NH_2):NH. *Thiodicyandiamidine.* White glistening prisms; m. sol. cold water.

Formation.—1. By digesting di-cyan-diamide with aqueous H_2S (Bamberger, *B.* 16, 1459).—2. By heating guanyl-urea with aqueous H_2S (B.).—3. From $CSCl_2$ and thio-urea at 110°.—4. In small quantity by the action of PCl_5 (1 mol.) on thio-urea (3 mols.) (Rathke, *B.* 11, 962).

Reactions.—Silver salts readily displace the S by O. On heating with ammoniacal $AgNO_3$ it is resolved into H_2S and di-cyan-diamide. When heated alone at 100° it changes to the isomeric guanidine sulphocyanide.

Salts.—$B''_2H_2C_2O_4$ 2aq : sparingly soluble crystalline pp.—$B''H_2SO_4{}^{\times}$: white silky needles. —B''HCl.

GUANYL-UREA $C_2H_6N_4O$ *i.e.* OC(NH_2).NH.C(NH_2):NH. *Di-cyan-di-amidine.*

Formation.—1. By evaporating a solution of di-cyan-di-amide $(CN)_2(NH_2)_2$ in dilute H_2SO_4 (Haag, *A.* 122, 25), and is therefore also formed by the action of dilute H_2SO_4 or H_3PO_4 on cyanamide (Baumann, *B.* 6, 1374).—2. By fusing guanidine carbonate (1 pt.) with urea (2 pts.) (Baumann, *B.* 7, 446, 1768).—3. By heating a mixture of carbamic ether (2 pts.) and guanidine carbonate (1 pt.) at 160° as long as alcohol distils over (Bamberger, *B.* 20, 68).—4. A mixture of guanidine hydrochloride and potassium cyanate is heated at 180° (Bamberger).

Preparation.—The base, prepared by any of the above processes, is ppd. from the aqueous solution of the product by $CuSO_4$ and NaOH. The resulting copper derivative is then decomposed by H_2S.

Properties.—Strongly alkaline crystals; absorbing CO_2 from the air. V. sol. water and alcohol. $KClO_3$ and HCl oxidise it to guanidine. Boiling baryta-water converts it into urea, CO_2, and NH_3. On evaporating a solution of guanyl-urea carbonate there is left guanidine carbonate, NH_3 and CO_2 having been given off.

Salts.—B'HCl ½aq : laminæ, v. sol. water and alcohol.—$B'_2H_2PtCl_6$: small orange crystals. —$B'HNO_3$: needles.—Aurochloride : long golden needles.—$B'_2H_2SO_4$ 2aq : long needles.—$B'H_2CO_3$: crystalline powder. S. ·67 at 18°.—$B'_2H_2C_2O_4$.

GUM. This term is applied to carbohydrates, whether produced by plants or animals, which are amorphous, insoluble in alcohol, but form a sticky liquid with water, in which they either dissolve or swell up greatly. By nitric acid the vegetable gums are oxidised to mucic and oxalic acids. They give no colouration with iodine either before or after treatment with conc. H_2SO_4. Boiling dilute H_2SO_4 converts them into glucose or a sugar $C_6H_{12}O_6$. Thus dextrose (glucose) is formed from lichenin; lævulose is formed from lævulin; galactose is formed from galactin, agar-agar, some kinds of gum arabic, and a gum in lucerne and other leguminous plants; while arabinose is formed from gum-arabic, cherry gum, gum tragacanth, and the gum in the cell walls of beet-root and poppies (Bauer, *J. pr.* [2] 30, 388). Gums are described under AGAR-AGAR, ARABIN, BASSORIN, CERASIN, DEXTRANE, DEXTRIN, GAMBOGE, GELOSE, GREVILLEA GUM, KAURI GUM, LACTOSIN, LÆVULANE, LÆVULIN, LICHENIN, MUCILAGE, PROTEÏDS, *Appendix* C, QUEBRACHO GUM, SHELLAC, SINISTRIN, TRITICIN.

GUM AMMONIAC. The dried sap of *Dorema ammoniacum.* It is partly soluble in water, but contains also an insoluble resin (Johnston, *A.* 44, 328; Hirschsohn, *J.* 1875, 859; Moss, *J.* 1873, 867). When fused with potash it gives resorcin and protocatechuic acid. The portion of gum ammoniac (from Morocco) soluble in alcohol gives by potash-fusion an acid $C_{10}H_{10}O_6$, which forms minute crystals, sl. sol. water, m. sol. alcohol, melting with decomposition at 265°, and giving with $FeCl_3$ a violet colouration (Goldschmiedt, *B.* 11, 850). HNO_3 acting on gum ammoniac forms tri-nitro-resorcin. Distillation with zinc-dust forms *m-* and *p*-xylene, *m*-ethyl-toluene, [2:1]$C_6H_4Et(OMe)$, and a hydrocarbon $C_{13}H_{20}$ (235°) which on oxidation with chromic mixture forms benzoic and acetic acids and resinous products (Ciamician, *B.* 12, 1663; *G.* 9, 813).

GUM, ANIMAL, *v.* Proteïds, *Appendix C.*

GUM ARABIC *v.* Arabin.

GUM BENZOÏN *v.* vol. i. p. 477.

GUM, BRITISH, *v.* Dextrin.

GUMMIC ACID $C_6H_{10}O_{10}$ (Reichardt). This name was applied by Fremy to arabin, but transferred by Reichardt (*A.* 127, 300) to an acid formed in the oxidation of glucose by Fehling's solution. Felsko (*A.* 149, 356; *Z.* [2] 5, 228), working under Reichardt's direction, gave the formula $C_6H_{16}O_{18}$, but according to Claus (*J. pr.* [2] 4, 63) gummic acid is more or less impure tartronic acid.

Metagummic acid *v.* Arabin and Cerasin.

GUM RESINS. The hardened milky juice which exudes from incisions in the stem or roots of some plants. They are partly soluble in water (gum) and part of the residue is soluble in alcohol (resin). *Examples*: asafœtida, aloes, galbanum, gamboge, gum ammoniac, myrrh, olibanum, opoponax, and scammony.

GUM SENEGAL *v.* Arabin.

GUN COTTON *v.* Cellulose.

GUNPOWDER. A mixture of charcoal, nitre, and sulphur, which when burnt produces large volumes of gases chiefly CO, CO_2, N, H, H_2S, and O (*v.* Dictionary of technical chemistry).

GURJUN BALSAM *v.* Wood oil.

GURJUNIC ACID *v.* Wood oil.

GUTTA PERCHA. A substance resembling caoutchouc obtained by boiling to dryness the milky sap which exudes from incisions in the bark of the *Isonandra Percha*, *Sapota Muelleri* (Bleekrode, *Rép. chim. app.* 1, 403), and *Bassia Parkii.*

Gutta percha is a brownish-red mass, S.G. ·98. It is a very bad conductor of electricity. It softens at about 48°, but never possesses the elastic character of caoutchouc. It is deposited from its solution in CS_2 in a very porous mass. Gutta percha is insol. water. It dissolves easily in benzene, CS_2, chloroform, and oil of turpentine. It is not attacked by solutions of HCl, KOH, or HF. Hot conc. H_2SO_4 carbonises it. HNO_3 converts it into a yellow resin.

According to Payen (*C. R.* 35, 109) gutta percha, purified by solution in CS_2, consists of three hydrocarbons: 'gutta' a portion insoluble in boiling alcohol, amounting to 75 to 82 p.c.; 'alban' a portion soluble in boiling, but insoluble in cold, alcohol, amounting to 19 to 14 p.c.; and a yellow resin 'fluavil,' soluble in cold alcohol, and amounting to 6 to 4 p.c. of the whole.

Gutta $C_{10}H_{16}$. Obtained by exhausting gutta percha with boiling alcohol and ether, dissolving the residue in chloroform, and ppg. by alcohol (Oudemans, *Rép. chim. app.* 1, 455; Von Baumhauer, *J. pr.* 78, 277; Adriani, *Z.* 1860, 496; Hofmann, *A.* 115, 297). White powder, cakes together and becomes transparent at 100°, begins to melt at 150°; at 180° an oil distils over, and at 280° it froths strongly. It is insol. alcohol and ether, sol. cold chloroform and CS_2, sol. hot benzene and oil of turpentine. After exposure to the air it becomes soluble in ether. Gutta is strongly attacked by ozonised oxygen. Conc. HClAq attacks it, apparently forming compounds containing chlorine. On dry distillation it behaves like caoutchouc, giving isoprene C_5H_8, caoutchene $C_{10}H_{16}$, heveene (Greville Williams, *C. J.* 15, 124), and a volatile acid. When exposed to air and light, especially at 25° to 30°, it is completely deprived of flexibility through oxidation (Hofmann, *C. J.* 13, 87; Adriani, *C. N.* 2, 227, 289, 313). Gutta percha may be kept for a long time unchanged under water or in the dark (W. A. Miller, *C. J.* [2] 3, 273).

Alban. White crystalline resin; best obtained by extracting gutta percha with ether, and boiling the resulting extract with alcohol to remove fluavil. Begins to melt at 100°, and is perfectly fluid and transparent at 180°. Insol. water, alkalis, and acids; v. sol. oil of turpentine, benzene, CS_2, ether, chloroform, and hot alcohol (Payen, *C. R.* 35, 109). According to Oudemans (*Rép. chim. app.* 1, 455) alban from Indian gutta percha may be represented by the formula $C_{10}H_{16}O$, and at 130° by $C_{20}H_{30}O$, and melts at 140°; S. (alcohol) ·51 in the cold; 5·4 at 78°.

Fluavil $C_{20}H_{32}O$. [42°] (Oudemans). Yellow resin; sol. alcohol, ether, benzene, oil of turpentine, CS_2, and chloroform, remaining as an amorphous mass when these solutions are evaporated. Conc. HClAq dissolves it without decomposition.

Gutta percha from *Bassia Parkii* resembles ordinary gutta percha in its physical properties, and has S.G. ·976. It is much less soluble in light petroleum, ether, HOAc, and oil of turpentine, but is equally soluble in CS_2, chloroform and benzene. It consists of gutta (91·5 p.c.), alban (6 p.c.), and fluavil (2·5 p.c.) (Heckel a. Schlagdenhauffen, *C. R.* 101, 1069).

GYROPHORIC ACID $C_{36}H_{36}O_{15}$. An acid obtained from two lichens, *Gyrophora pustulata* and *Lecanora tartarea*, collected in Norway for the manufacture of archil. The lichen is macerated with milk of lime, and the filtrate ppd. by HCl; the pp. is dissolved in boiling alcohol, containing animal charcoal, from which the acid crystallises on cooling (Stenhouse, *P. T.* 1849, 393). Small soft crystals; nearly insol. water, v. sl. sol. ether and cold alcohol, m. sol. boiling alcohol. Its solutions do not redden litmus. Boiling aqueous KOH or baryta resolve it into CO_2 and orcin. Bleaching-powder reddens its solution. When mixed with NH_3 and exposed to the air it forms a purple substance. Boiling alcohol forms orsellic ether. Gerhardt (*Traité*, 3, 818) regarded gyrophoric acid as identical with lecanoric or evernic acid.

H

HÆMATEÏN *v.* Hæmatoxylin.

HÆMATIN *v.* Hæmoglobin.

HÆMATO-CRYSTALLIN *v.* Hæmoglobin.

HÆMATO-GLOBULIN *v.* Hæmoglobin.

HÆMATOIDIN *v.* Hæmoglobin.

HÆMATOIN *v.* Hæmoglobin.

HÆMATOLIN *v.* Hæmoglobin.

HÆMATO-PORPHYRIN *v.* Hæmoglobin.

HÆMATO-PORPHYROIDIN *v.* Hæmoglobin.

HÆMATOXYLIN $C_{16}H_{14}O_6$. *Hæmatin.* A colourless crystalline substance from which the colouring matter of logwood (*Hæmatoxylon campechianum*) is derived (Chevreul, *A. Ch.* [2] 80, 128; 82, 53, 126; Golfier-Besseyre, *A. Ch.* [2] 70, 272; Erdmann, *A.* 44, 292; Hesse, *J. pr.* 75, 216; *A.* 109, 332). Prepared by leaving the commercial extract of logwood, previously mixed with sand, in contact with five times its volume of wet ether for several days, with frequent shaking; the extract is evaporated, and the residue recrystallised from water containing a little ammonium sulphite. Dimetric crystals (containing 3aq). When a supersaturated solution is allowed to stand in the cold it deposits hemihedral trimetric crystals (containing aq). The monohydrate is also obtained in granular crystals by pouring a solution that has been saturated at 100° into a cold vessel containing a small quantity of a solution of acid ammonium sulphite. Hæmatoxylin is sl. sol. cold water, v. sol. alcohol and ether. It dissolves in a saturated solution of borax more easily than in pure water, the solution being neutral or slightly acid, and exhibiting a bluish fluorescence. Alcohol does not ppt. borax from this solution. From the solution in borax the hæmatoxylin is ppd. by acids in the monohydrated form, and by salts (*e.g.* NaCl, KCl, NH_4Cl, K_4FeCy_6, and HNH_4SO_3) as an amorphous mass. Hæmatoxylin dissolves in warm $Na_2S_2O_3$ forming a purple liquid from which it is deposited on cooling in the amorphous form. It also dissolves freely in Na_2HPO_4, the solution remaining alkaline. Hæmatoxylin has a sweet taste, resembling liquorice. Its solutions are dextrorotatory, $[\alpha] = 92{\cdot}5°$ in a 1 p.c. solution. It reduces Fehling's solution and ammoniacal $AgNO_3$ in the cold. An aqueous solution of hæmatoxylin is not altered by contact with pure air or oxygen, but, if the slightest trace of ammonia be present, the liquid acquires a red colour due to hæmateïn (*v. infra*). Thus if the solution is boiled in a glass vessel it becomes purple by dissolving alkali from the glass (Maschke, *B.* 7, 1535; *Ar. Ph.* [3] 6, 34; Mitchell, *Am. Ch.* 6, 91). HNO_3 oxidises it at first to hæmateïn, but ultimately to oxalic acid. H_2SO_4 and HCl have but little action on it. Hæmatoxylin dissolves in alkalis and alkaline carbonates forming a purple solution, the colour being destroyed by acids (Wildenstein, *Fr.* 2, 9). Baryta-water added to a solution of hæmatoxylin freed from air by boiling forms a white pp. which turns blue if exposed to air. Basic and normal lead acetates give a white pp. turned blue in air; cupric acetate gives a greenish-grey pp. which soon becomes dark-blue with a coppery lustre. $SnCl_4$ gives a rose-coloured pp. Alum colours the solution red but gives no pp. $BaCl_2$ colours the liquid red, and then forms a red pp. $AuCl_3$ is reduced by hæmatoxylin. Ammonium vanadate gives a blue-black colour (Wagner, *D. P. J.* 223, 631). According to Schützenberger a. Paraf (*Z.* 1862, 42) the violet solution of hæmatoxylin in ammonia may be decolourised by heating for 48 hours at 100° in an exhausted tube; the colourless product, called 'hæmatinamide' is reoxidised on exposure to air, becoming violet. Resorcin and pyrogallol are among the products of the dry distillation of hæmatoxylin (R. Meyer, *B.* 12, 1392). Potash-fusion gives pyrogallol and formic acid (Erdmann a. Schultz, *A.* 216, 240). Sodium-amalgam or zinc and dilute H_2SO_4 do not reduce hæmatoxylin (Reim, *B.* 4, 329). Chlorine, bromine, PCl_5, and HI yield resinous products. According to Frébault (*J. Ph.* [4] 23, 338) the red colour of alkaline solutions of hæmatoxylin is destroyed by iodine.

Penta-acetyl derivative $C_{16}H_9Ac_5O_6$. [166°]. From hæmatoxylin and AcCl (Erdmann a. Schultz, *A.* 216, 232; *cf.* Reim, *B.* 4, 331). Silky crystalline tufts; becomes coloured in moist air.

Bromo-hæmatoxylin $C_{16}H_{13}BrO_6$. Dissolves in aqueous KOH or NaOH with a blue colour, in aqueous NH_3 with a red colour.

Pent-acetyl derivative $C_{16}H_8BrO_6Ac_5$: [210°]; fine colourless needles; sol. alcohol, acetic acid, benzene and chloroform. Formed by adding bromine to a cold acetic acid solution of penta-acetyl-hæmatoxylin (Buchka, *B.* 17, 683).

Di-bromo-hæmatoxylin $C_{16}H_{12}Br_2O_6$. From hæmatoxylin and Br in HOAc (Dralle, *B.* 17, 373). Deep-red needles. Decomposes above 120°. Its aqueous solution is brownish-red.

Penta-acetyl derivative $C_{16}H_7Br_2Ac_5O_6$. From penta-acetyl-hæmatoxylin and Br in HOAc at 110° (D.). Crystals; decomposes above 180° without melting.

Hæmatoxylin-phthaleïn $C_{40}H_{30}O_{14}$. Prepared by heating hæmatoxylin with phthalic anhydride (Letts, *B.* 12, 1651). Brown amorphous mass, insol. water, sol. alkalis, forming a purple-red solution.

Hæmateïn $C_{16}H_{12}O_6$. S. ·06 at 20°; S. (ether) ·013 at 20°.

Preparation.—Extract of logwood is dissolved in hot water and, after cooling, NH_3 in slight excess is added. The solution is exposed to air which changes hæmatoxylin to hæmateïn, the ammonia compound of which is ppd. This pp. (40 g.) is dissolved in hot water (1000 g.) containing acetic acid (100 c.c.), and the solution is filtered. On cooling crystals of hæmateïn appear (Hummel a. A. G. Perkin, *C. J.* 41, 367; *cf.* Halberstadt a. Reis, *C. J.* 41, 368; *B.* 14, 611).

Properties. — Microscopic reddish-brown plates with yellowish-green lustre. Sparingly soluble in water, alcohol, ether, and acetic acid.

Forms with NH_3 a brown-violet solution, with conc NaOH a purple-blue solution; in air these liquids turn red and finally brown. Freely soluble in conc. HClAq. It dissolves in alkaline bisulphites, and is reppd. by hot dilute H_2SO_4.

Reactions.—1. Cold conc. H_2SO_4 dissolves it. On pouring the solution into water a reddish-brown pp. of altered hæmatein is formed. On adding glacial acetic acid to the solution in cold conc. H_2SO_4 an orange crystalline powder **iso-hæmatein sulphate**, $C_{16}H_{11}O_5.SO_4H$, is ppd. This body is converted by dilute (80 p.c.) alcohol into lustrous orange-red crystals of $(C_{16}H_{12}O_6)_2C_{16}H_{11}O_5SO_4H$.—2. With HCl at 100° it forms orange-red needles of **iso-hæmateïn-chlorhydrin** $C_{16}H_{11}O_5.Cl$, soluble in water with decomposition and separation of HCl. Its solution is orange. With alcoholic KOH it gives a reddish-violet solution. Conc. H_2SO_4 converts it into iso-hæmateïn sulphate.—3. With HBr it gives a corresponding bromhydrin, $C_{16}H_{11}O_5Br$. 4. Decolourised by Zn and dilute H_2SO_4, but not reduced to hæmatoxylin thereby. Boiling aqueous SO_2 behaves in like manner (Reim).—5. AcCl gives no acetyl derivative.

Ammonium derivative $C_{16}H_{10}(NH_4)_2O_6$: violet-black grains; forming a purple solution in water, and a brownish-red solution in alcohol, gives off NH_3 over H_2SO_4.

Iso-hæmatein $C_{16}H_{12}O_6$. A solution of the chlorhydrin $C_{16}H_{11}O_5Cl$ gives with Ag_2O a solution which, on evaporating, leaves amorphous iso-hæmatein with green lustre.

Properties.—Solution in NaOH is red-violet, in NH_3 is dull red-purple; with ammonic sulphide a red-purple pp. is got (hæmateïn is nearly decolourised by this reagent). Lead acetate gives a red-purple pp.

Iso-hæmateïn compounds dye with alumina chocolate-red, with iron, slate to black. The colours are faster than those of hæmatein. The generation of *iso*-hæmateïn in place of ordinary hæmatein from $C_{16}H_{11}O_5Cl$ is peculiar. Perhaps it is $(C_{16}H_{12}O_6)_3$ as indicated by the sulphate.

(β)-**Hæmateïn** $C_6H_{12}O_6$ 3aq. Deposited as small brownish-red tufts from an ethereal solution of hæmatoxylin to which a few drops of HNO_3 have been added (Reim, *B.* 4, 331). It is more soluble in boiling water than hæmatein (Erdmann a. Schultz, *A.* 216, 236). It is reconverted into hæmatoxylin by boiling with aqueous SO_2 or with zinc and dilute H_2SO_4. AcCl gives an acetyl derivative [216°–219°].

HÆMIN *v.* HÆMOGLOBIN.

HÆMOCHROMOGEN *v.* HÆMOGLOBIN.

HÆMOCYANIN *v.* PROTEÏDS.

HÆMOGLOBIN (syn. *Hæmato-globulin, hæmato-crystallin*). This pigment composes from 86-90 per cent. of the solid constituents of the red blood corpuscles of vertebrates; it is also found in the blood plasma of many invertebrate animals, and in the red corpuscles of the hæmo-lymph of a few invertebrates (Lankester). For a complete list of the animals in the blood of which it has been described *v.* Halliburton (*J. Physiol.* 6, 332). It is found in the muscle-plasma of most animals, even when none occurs in the blood, as in some invertebrates (Lankester, *Pflüger's Archiv*, 4, 315); it is most abundant in the red muscles of rodents. It is also found in the nerve-cells of *Aphrodite aculeata* (Gamgee, *Physiol. Chem.* 420).

Preparation.—Leidig (*Zeits. f. wiss. Zool.* 1, 116), Reichert (*Müller's Archiv*, 1849, 197), Kölliker (*Zeits. f. wiss. Zool.* 1, 216) first observed that blood from different sources deposited crystals of a red colour. Funke (*Zeit. f. rat. Med.* N. F. 1, 184; 2, 204, 288) recognised that they consisted of the red pigment of the blood. Lehmann (*Sitz. W.* 46, 65), Lang (*ibid.*), and Preyer (*Die Blutkrystalle*, Jena, 1871) have also worked at the subject. The principal methods for preparing these crystals will be found in detail in Gamgee's *Physiol. Chem.* 85–88. The crystals may be obtained with ease from the blood of some animals (rat, guinea pig) by simply adding water to the blood; this first dissolves the hæmoglobin from the corpuscles, and without further treatment the crystals form in a few minutes. A very excellent method consists in adding to the defibrinated blood one-sixteenth of its volume of ether, or a mixture of alcohol and ether; on shaking the mixture the corpuscles dissolve, forming a lake-coloured fluid, and in a period varying in different animals from a few minutes to three days, a thick magma of crystals is formed, which may be purified by washing with 25 p.c. alcohol, and by re-crystallisation. In other methods the corpuscles are broken up by repeatedly freezing and thawing the blood with or without the previous addition of a quarter of its volume of alcohol, and crystals are thus obtained. The blood of the mouse is said to crystallise when drawn, without any further treatment; in septic diseases in man, or by adding putrid serum to the blood, there is the same crystalline tendency (C. J. Bond, *Lancet*, Sept. 10 and 17, 1887). The crystals obtained by all these methods are microscopic; larger crystals are formed by sealing blood which has stood in the air for twenty-four hours in narrow glass tubes and keeping them for some days at 37°C. On then emptying their contents into watch glasses the crystals form (Gschleidlen, *Physiol. Methodik*, 361). For microscopical investigation a very convenient method is to mount a drop of blood in Canada balsam, and the crystals separate in a few minutes (Stein, *Virchow's Archiv*, 97, 483). The crystals in all these cases are generally spoken of as hæmoglobin crystals; it would be more correct to speak of them as crystals of oxy-hæmoglobin, the loose combination of oxygen and hæmoglobin that exists in arterial blood. Crystals of pure or venous hæmoglobin have, however, been obtained by Hüfner and by Nencki and Sieber (*Chem. Soc. Abst.* 1886, p. 482).

Crystalline form.—Not only does the hæmoglobin of different animals differ in the readiness with which it crystallises, and in its solubility in water, but also in crystalline form. As obtained from the majority of animals, the crystals are prisms or plates belonging to the rhombic system; the exceptions to this rule are the guinea-pig, in which the crystals were at first supposed to be regular tetrahedra (Kunde, *Zeits. für rat. Med.* N. F. 2, 276), but have since been shown by Von Lang to be rhombic tetrahedra. In birds the crystals are often tetrahedral. These crystals are doubly refracting and pleochromatic. In three animals, the squirrel (Kunde), hamster (Preyer), and mouse (Bojanowski), six-sided plates have been described. The statement regarding mouse's crystals is, however, erroneous. Rhombohedra have been obtained from hamster's blood. Occasionally six-sided plates are obtained from rat's blood (Halliburton, *Quart. Jour. Mic. Sci.* 1887, 190). These crystals, if they are lying flat, appear dark between crossed nicols, and therefore belong to the hexagonal system. The amount of water of crystallisation varies greatly in the crystals from different sources, and it is probably owing to this that the difference in crystalline form is due (Hoppe-Seyler, *Physiol. Chem.* 377 ; C. Bohr, *Untersuch. über d. Sauerstoffaufnahme des Blutfarbstoffes*, Kopenhagen, 1885; Halliburton, *l.c.*).

Composition.—Hæmoglobin differs from most of the other proximate constituents of the body in containing iron. Preyer's formula for it is $C_{600}H_{960}N_{154}FeS_3O_{179}$. Determinations of the sulphur by other observers were, however, contradictory; on this ground Lehmann and others advanced the theory that hæmoglobin is not a chemical unit, but consists of a colouring matter, hæmatin, which contains the iron, mechanically mixed with a crystallised proteïd. A seeming confirmation of this theory was advanced by Struve (*Zeit. Prakt. Chem.* 1884), who extracted hæmatin from the crystals by alcoholic ammonia, leaving them colourless. Zinoffsky (*Zeit. Physiol. Chem.* 10, 16) points out, however, that alcoholic ammonia is a powerful reagent, and shows that the conflicting results as to the quantity of sulphur present are due to bad methods of preparation of the hæmoglobin. Adopting the ether method of preparing the crystals (for the modifications of the method as already described the original paper must be consulted), he found that the empirical formula for hæmoglobin is $C_{712}H_{1130}N_{214}S_2FeO_{245}$. By heat, or by the action of strong acids or alkalis, hæmoglobin is decomposed into hæmatin ($C_{68}H_{70}N_8Fe_2O_{10}$) and a proteid or mixture of proteïds known under the name Globin (for the properties of globin *v.* PROTEIDS).

Properties.—Though crystallisable, hæmoglobin is not diffusible; its colour differs with the amount of oxygen with which it is combined; the pure pigment has a purplish tinge; the oxygenated condition in which it usually exists is a yellowish-red. In both conditions solutions of the pigment show with the spectroscope typical absorption bands. The spectrum of oxyhæmoglobin varies with the concentration of the solution; in addition to a certain amount of absorption of both ends of the spectrum there are two typical bands between the D and E lines, the α band has for its centre the wave-length 579; the β band, which is wider and less well-defined, has its centre at wave-length 553 (Hoppe-Seyler) (see spectrum, 2). Stokes first showed that on the addition of reducing agents to such a solution the colour of the liquid changes to that of hæmoglobin, and this has only one absorption band, which occupies approximately the light space between the two bands of oxyhæmoglobin (see spectrum, 3). The most convenient reducing agent to use is 'Stokes's reagent,' which must always be freshly prepared by adding a small quantity of citric or tartaric acid to a solution of ferrous sulphate, and then ammonia till the reaction is alkaline. Or a solution of ammonium sulphide, or a stream of a neutral gas like hydrogen may be used. If the solution which shows the spectrum of reduced hæmoglobin be agitated with the air or oxygen it once more becomes brighter in colour, and shows the two bands of oxyhæmoglobin. This spectroscopic test is the one most usually applied for the identification of hæmoglobin. The bands are still perceptible when the solution contains only 1 part of hæmoglobin in 10,000 of water. Another test frequently used is to obtain crystals of hæmin (*q. v.*). The crystals of oxy-hæmoglobin dried *in vacuo* still retain 3-4 per cent. of water of crystallisation, which is driven off by heating to 110°-120°C. The dried substance may be heated to 100°C. without undergoing decomposition.

Hæmoglobin gives all the tests of proteïds. Oxyhæmoglobin has the power of decomposing hydrogen peroxide. Preyer finds that 1 grm. of hæmoglobin can link to itself 1·67 c.c. of respiratory oxygen; Hüfner (*Zeit. physiol. Chem.* i. 317) gives approximately the same figure; the theory of A. Schmidt that hæmoglobin has the power of ozonising the oxygen it thus links to itself has been disproved by Pflüger (*Pflüger's Archiv*, 10, 252).

Estimation of hæmoglobin.—(*a*) *From the amount of iron*; dry hæmoglobin contains 0·42 p.c. of iron. A weighed quantity of blood is calcined; the ash is exhausted with hydrochloric acid to obtain ferric chloride, which is transformed into ferrous chloride, and titrated with potassium permanganate. (*b*) *Colorimetrically* (Hoppe-Seyler; Rajewsky; Malassez): the most convenient instrument is Gower's hæmoglobinometer (*Lancet*, vol. ii. 1878, p. 822). (*c*) Spectroscopically, by comparing the amount of absorption of light with that of a standard solution (*v.* Hüfner, *l.c.*, Preyer, *l.c.* On the Spectrophotometer, *v.* S. Lea, *J. Physiol.* 5, 239). The absorption coefficient of oxyhæmoglobin increases each time it is recrystallised (F. Krüger, *Zeit. Biol.* 24, 471). *V.* also Fleischl, *Maly's Jahrb.* xv. 149; Otto, *ibid.* 146; Quinquaud and Brany, *ibid.* 151; E. Lambling, *Arch. de Physiol.* [4] 12, 1.

Compounds.—**Oxyhæmoglobin.** This loose combination of oxygen and hæmoglobin is formed in the pulmonary or branchial capillaries, and forms the oxygen carrier to the tissues to which it goes, and where it parts with its oxygen, returning in the venous blood for a fresh supply. As already stated, this compound can also be made artificially from hæmoglobin when in solution outside the body. For the most recent work regarding the dissociation of oxyhæmoglobin *v.* Hufner, *Zeit. physiol. Chem.* 12, 568; 13, 285.

Carbonic oxide hæmoglobin is formed when carbonic oxide is breathed instead of, or mixed in undue proportions with, oxygen. The formation of this substance is the cause of death in poisoning from this gas, which is contained, for instance, in the fumes of burning charcoal. The compound has a bright cherry-red colour, is much more stable than oxyhæmoglobin. Its absorption bands are very like those of oxyhæmoglobin, but they are situated rather nearer to the blue end of the spectrum (see spectrum, 4);

the addition of reducing agents does not cause any reduction to the condition of hæmoglobin. It can be obtained in a crystalline condition, and the crystals are of the same form as those of oxyhæmoglobin, but are more stable. For other tests for CO hæmoglobin *v.* Hoppe-Seyler (*Zeit. physiol. Chem.* 2, 131), Salkowski (*ibid.* 12, 227), Katayama (*Virch. Arch.* 1888, p. 53). **Nitric oxide hæmoglobin** forms similar crystals, and in solution has an absorption spectrum resembling those of the two preceding substances. These three compounds are isomorphous, one molecule of each gas being replaceable by one of either of the other two, and is presumably linked with one molecule of hæmoglobin. Compounds of hæmoglobin with acetylene and with hydrocyanic acid have been also described (Hoppe-Seyler, *Med. Chem. Unters.* 2, 207).

Methæmoglobin. This is occasionally found in the body; *e.g.* in sanguineous effusions and in the urine. Our chief knowledge of it is, however, obtained from preparations of it from hæmoglobin made artificially. By simply allowing blood to stand for some days it turns acid, and of a brownish tint, and its hæmoglobin is found to be wholly or partially transformed into methæmoglobin. It may also be obtained by adding oxidising agents to blood, or to solutions of oxyhæmoglobin or hæmoglobin, *e.g.* potassium permanganate, potassium ferricyanide, nitrites, &c. (for a list of such substances *v.* G. Hayem, *Compt. Rend.* 102, 698). On the subsequent addition of reducing agents, first oxyhæmoglobin and then hæmoglobin is again formed. This is seen best by spectroscopic examination. The reduction, however, cannot be effected by simple mechanical means like a vacuum or a stream of hydrogen. The typical band of methæmoglobin is situated in the red between the C and D lines, rather nearer to the former (see spectrum, 5); in a dilute solution three other bands are seen (see spectrum, 6). Methæmoglobin may also be obtained in a crystalline form (guinea-pig, tetrahedra; rat, squirrel, horse occasionally, hexagonal; in most other animals, rhombic). A ready method of obtaining these crystals for microscopic examination is by shaking a few drops of amyl nitrite with a few c.c. of defibrinated blood, and then on mounting on a slide a drop of the mahogany-coloured mixture that results, crystals appear in a few minutes (Halliburton, *Quart. J. of Mic. Sci.* 1887, 201). Other methods consist in adding a nitrite and alcohol, and freezing (Gamgee, *Phil. Trans.* 1868, 589, where they are described, however, as a compound of hæmoglobin with nitrous acid), or ferricyanide of potassium may be used instead (Hüfner, *Zeit. Physiol. Chem.* 8, 366). Sorby considered methæmoglobin as a peroxyhæmoglobin (*Quart. J. Mic. Sci.* 1870, 400). Hoppe-Seyler on the contrary believed that it was a suboxyhæmoglobin, intermediate between oxyhæmoglobin and hæmoglobin, but that the oxygen was more firmly combined than it is in oxyhæmoglobin; he found by removing some of the oxygen from oxyhæmoglobin by means of an air-pump, or by nascent hydrogen, that methæmoglobin was formed (*Zeit. Physiol. Chem.* 2, 150). Hüfner and Külz (*ibid.* vol. vii.), having been able to obtain pure crystallised methæmoglobin, have found that the oxygen in both that compound and in oxyhæmoglobin are equal in amount but combined more feebly in the latter.

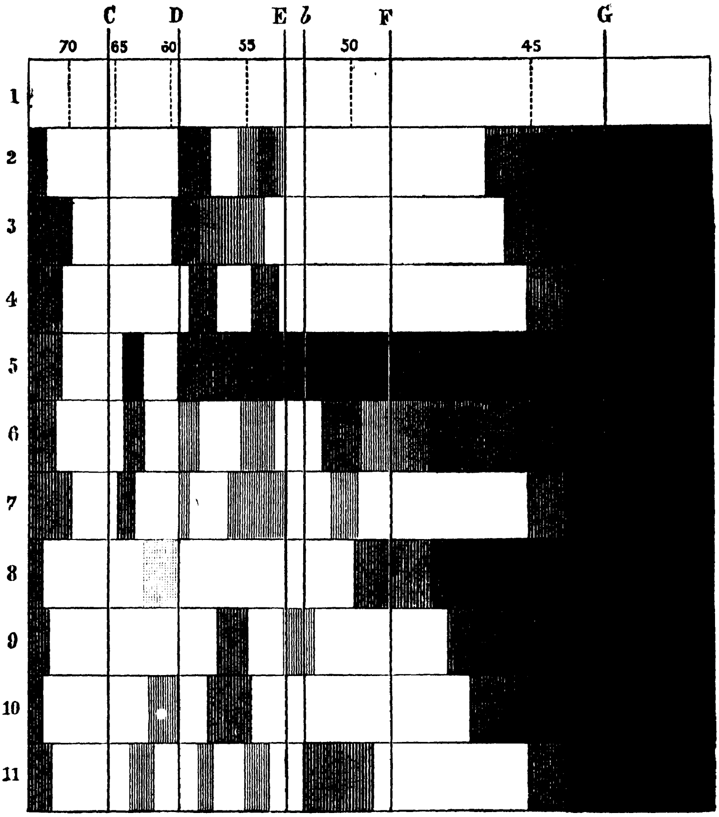
Parahæmoglobin.— This was described by Nencki and Sieber (*Arch. Exper. Path. u. Pharmakol.* 10, 331; *Ber.* 18, 2126) as a special compound; but is regarded by Hoppe-Seyler (*Zeit. Physiol. Chem.* 10, 331) as a coagulation product brought about by the action of alcohol

DERIVATIVES OF HÆMOGLOBIN.

Hæmatin ($C_{68}H_{70}N_8Fe_2O_{10}$) is the brown pigment obtained by the action of acids or alkalis on hæmoglobin in the presence of oxygen. This decomposition occurs more readily in the hæmoglobin of some animals (dog, man, &c.) than in others (herbivora) (Krüger, *Zeit. Biol.* 24, 318). It may be obtained by adding acetic acid to blood, and then extracting the hæmatin with ether. Mac-Munn recommends the following method: blood clot is extracted with rectified spirit containing sulphuric acid (1 in 17); the extract is filtered and agitated with chloroform, which assumes a reddish-brown colour and is separated, filtered, and washed with water to remove the acid. On evaporating the chloroform the hæmatin is obtained as a bluish-black powder (*J. Physiol.* 6, 22). Hoppe-Seyler obtains hæmatin from hæmin, which is first dissolved in solution of potassium hydrate, and the hæmatin ppd. by hydrochloric acid (*Med. Chem. Unters.* 4, 523). Hæmatin dissolved in an acid solution shows four absorption bands (4 banded hæmatin or hæmatoin); first, one between the C and D lines, this is the most distinct and is nearer to the C line than the corresponding band of methæmoglobin; secondly, a faint narrow band close to D; thirdly, two much broader bands, one between D and E and another between E and F (see spectrum, 7). When hæmatin is dissolved in an alkaline solution (alkaline hæmatin) one band only is seen, viz. a faint shading on the red side of the D line (see spectrum, 8). There is, however, a large absorption of the violet end of the spectrum. On adding reducing agents to alkaline hæmatin, the bands of reduced hæmatin (hæmochromogen) are seen.

Hæmatin is insol. water, ether, alcohol, and dilute acids; v. sol. solutions of caustic alkalis, and hot alcohol holding sulphuric acid in solution. It can be heated to 180° without undergoing decomposition; at a temperature above this it burns and evolves hydrocyanic acid, and leaves an ash of oxide of iron amounting to 12·6 p.c.

Hæmochromogen ($C_{34}H_{37}N_4FeO_5$). When hæmoglobin is decomposed in the absence of oxygen, instead of hæmatin, a substance of a purple colour called hæmochromogen is produced, which is converted into hæmatin in contact with oxygen. A solution of oxyhæmoglobin is freed from oxygen by a stream of hydrogen, and then mixed with an alcoholic solution of sulphuric acid or caustic potash (Hoppe-Seyler, *Med. Chem. Unters.* 4, 523, 377; *Zeit. physiol. Chem.* 1, 138). This substance is identical with the reduced hæmatin of Stokes, obtained by adding a reducing agent like ammonium sulphide to alkaline hæmatin in the presence of proteids (Jäderholm, *Maly's Jahrb.* 6, 85; Linossier, *C. R.* 104, 1296). Hæmochromogen shows two absorption bands, one midway between the D and E lines, and the other occupying the space between E and *b* (see spectrum, 9). In testing for blood where the hæmoglobin has undergone decomposition, as in old stains, the most readily obtained spectrum is that of hæmochromogen. The stained fabric is extracted with a little caustic alkali, and ammonium sulphide or hyposulphite of soda added; the two bands of hæmochromogen or in weak solutions the better marked band (that between D and E) then appear.



1. Solar spectrum.
2. Spectrum of oxyhæmoglobin (0·37 p.c. solution). First band, λ 589–564; second band, 555–517.
3. Spectrum of hæmoglobin. Band, λ 597–535.
4. Spectrum of CO hæmoglobin. First band, λ 583–564; second band, 547–521.
5. Spectrum of methæmoglobin (concentrated solution).
6. Spectrum of methæmoglobin (dilute solution). First band, λ 647–622; second band, λ 587–571; third band, λ 552–532; fourth band, λ 514–490.
7. Spectrum of acid hæmatin (ethereal solution). First band, λ 656–615; second band, λ 597–577; third band, λ 557–529; fourth band, λ 517–488.
8. Spectrum of alkaline hæmatin. Band from λ 630–562.
9. Spectrum of hæmochromogen (reduced hæmatin). First band, λ 569–542; second band, λ 535–504.
10. Spectrum of acid hæmatoporphyrin. First band, λ 607–593; second band, λ 585–536.
11. Spectrum of alkaline hæmatoporphyrin. First band, λ 633–612; second band, λ 589–564; third band, λ 549–529; fourth band, λ 518–488.

The above measurements (after MacMunn) are in millionths of a millimetre. The liquid was examined in a layer one centimetre thick. The edges of ill-defined bands vary a good deal with the concentration of the solution.

Hæmatoporphyrin ($C_{68}H_{74}N_8O_{12}$). This pigment is obtained by adding blood or pure hæmatin to conc. sulphuric or hydrochloric acid; the action of the acid is to remove the whole of the iron in the condition of a ferrous salt. It can be ppd. by adding water to this compound. The pp. is soluble in water and in alkaline leys. The acid solution exhibits spectroscopically one band immediately below D, and another nearly intermediate between D and E (see spectrum, 10). The alkaline solution has four bands: one between C and D, two between D and E, and a fourth, which extends through 4/5 of the space between *b* and F (see spectrum, 11). A second iron-free derivative has been obtained from hæmatin by Hoppe-Seyler; he calls it *hæmatolin* ($C_{68}H_{78}N_8O_7$), it is nearly insoluble in sulphuric acid and caustic alkalis. Various derivatives of hæmatoporphyrin (hæmatoporphyroidin, isohæmatoporphyrin, &c.) are described by Nobel (*C. C.* 1887, 538). Hæmatoporphyrin occurs as a natural pigment in many invertebrates; *e.g.* in the dorsal streak of the earth-worm. It is probably derived here not from hæmoglobin, but from histohæmatins which occur in these animals, and which yield many of the decomposition products of hæmoglobin (MacMunn, *J. Physiol.* 8, 381). A derivative called uro-hæmatoporphyrin may occur in morbid human urine (MacMunn, *J. Physiol.* 10, 71).

Hæmin. *Hydrochloride of Hæmatin.* This is obtained for microscopical examination by boiling blood with glacial acetic acid and a crystal of sodium chloride (fresh blood contains, however, sufficient sodium chloride) on a slide; on cooling, rhombic crystals of a dark-brown colour separate (Teichmann); this is one of the best tests for blood. It has been prepared on a large scale by Hoppe-Seyler, who ascribes to it the formula $C_{68}H_{70}N_8Fe_2O_{10}2HCl$. Similar crystalline compounds are obtainable in which hydrobromic and hydriodic acids respectively take the place of HCl in the above formula (V. D. Harris, *Brit. Med. J.* 1886, 2, 103). Nencki a. Sieber (*Ber.* 17, 2267; 18, 392; *Monatschr.* 9, 115; *Arch. f. exp. Path. und Pharmak.* 24) ascribe to hæmatin the formula $C_{32}H_{32}N_4FeO_4$; and say hæmin crystals are composed of the hydrochloride of its anhydride $C_{32}H_{30}N_4FeO_3.HCl$. Their formula for hæmatoporphyrin is $C_{32}H_{36}N_4O_6$. Of this they describe an anhydride and a crystalline hydrochloride. It is isomeric with bilirubin.

Cyan-hæmatin. A compound with this name is said to be formed when potassium cyanide is added to an ammoniacal solution of pure hæmatin. It exhibits spectroscopically one band extending from D and E, and split into two by reducing agents.

Nitric oxide Hæmatin.—This is produced by passing nitric oxide into an alcoholic solution of hæmatin. Its absorption bands resemble those of oxyhæmoglobin (Linossier, *C. R.* 101, 1296).

Hæmatoidin. Everard Home (*A Short Tract on the Formation of Tumours*, London, 1830) first described certain microscopic crystals in old extravasations of blood; *e.g.* in apoplectic clots; to these Virchow (*Virch. Archiv*, 1, 383) gave the name hæmatoidin, and recognised that they were derived from the colouring matter of the blood. The same substance occurs sometimes in an amorphous condition. The crystals have also been found in the urine (*v.* Recklinghausen, Landois). The crystals are identical in form with those of bilirubin, the chief colouring matter of human bile, and give Gmelin's colour reaction with fuming nitric acid. It has the same formula $C_{32}H_{36}N_4O_6$. Neither hæmatoidin nor bilirubin show spectroscopic bands, but absorb the violet end of the spectrum powerfully. Although Holm (*J. pr.* 100, 142) and Preyer (*Die Blutkrystalle*, 187) deny the identity of the two substances, Salkowski (*Med. Chem. Unters.* 3, 436) and the majority of physiological chemists are, however, now of the opinion that the two are identical. Holm and Preyer probably mistook the lipochrome (lutein) of the cow's ovary for hæmatoidin (Thudichum, *Proc. R. S.* 17, 255).

Other animal pigments. Bilirubin and the other colouring matters of the bile, stercobilin, the pigment of the fæces, certain urinary pigments, melanin, the black pigment of the skin, retina, and of melanotic sarcomata, are all probably derived from hæmoglobin. The allied pigments myo-hæmatin and the histo-hæmatins will be described under MUSCLE. W. D. H.

HALOGEN ELEMENTS. The four elements, F, Cl, Br, and I are classed together under the name *halogens*, or salt-formers. The name was given by Berzelius (*Lehrbuch*, 1, 266 [5th ed.]) to those non-oxygenated radicles, simple or compound, which combine with metals to form salts. Berzelius regarded all salts as formed by the union of a positive and a negative radicle. He applied the name *salt-former* to the negative radicles, more especially to those which do not contain oxygen, and yet more particularly to the simple radicles F, Cl, Br, I, and the compound radicle cyanogen. The nomenclature has been maintained as regards the elements F, Cl, Br, and I. The binary compounds of these elements are usually called *haloid salts.* This name was also introduced by Berzelius; he used it to distinguish salts formed by the union of metals with F, Cl, Br, I, or CN from salts formed by the union of two radicles, each of which contained a common element, *e.g.* oxygen-salts, sulphur-salts, selenion-salts, &c.

The halogens are found in combination very widely distributed. Metallic chlorides are very numerous; bromides, iodides, and fluorides occur in smaller quantities. The elements themselves are scarcely found in the free state in nature; iodine is said to exist in minute quantities in sea water. Fluorides of all elements are known except Br, C, Cl, N, O, and some ten or twelve metals (mostly rare metals which have not been thoroughly examined); chlorides of all elements except F have been isolated; bromides of almost all elements except F and O are known; and iodides of all, or almost all, elements except F have been obtained.

The compounds of the halogen elements show resemblances both in composition and properties. If X = F, Cl, Br, or I, the chief metallic halogen compounds may be grouped under the forms:—

(1) MX; M = alkali metal, Ag, Cu, or Au; also Hg and Tl.

(2) MX_2; M = Be, Mg, Ca, Zn, Sr, Cd, Ba, Hg; also Cu; In; Sn, Pb; Fe, Ni, Co; the Pt metals.

(3) MX_3; M = Al, Ga, In, Tl; As, Sb, Bi; Fe, Cr.

(4) MX_4; M = Ti, Ge, Zr, Sn, Ce, Pb, Th, Mo, U; the Pt metals.

(5) MX_5; M = Nb, Sb, Di, Ta; Mo, W.

(6) MX_6; M = W.

The non-metallic halogen-compounds for the most part belong to the following forms:—

(i.) MX; M = H.

(ii.) MX_2; M = S, O, Se, Te.

(iii.) MX_3; M = B, N, P, As.

(iv.) MX_4; M = C, Si, Te.

(v.) MX_5; M = P.

The resemblances in the composition of the halogen-compounds are further brought out by the formulæ of oxyacids. These oxyacids for the most part belong to the four classes HXO, HXO_2, HXO_3, HXO_4; but no oxyacid of F has yet been isolated.

The halogens are all strongly electronegative; none of them replaces the hydrogen of acids to form salts. They combine directly with very many elements, and much heat is usually produced in the process. F is especially energetic in its reactions; it reacts with cold water to form ozonised O and HF, whereas Cl only reacts rapidly with water at a red heat, and the reactions of Br and I with water at high temperatures are very slow.

A comparison of the binary compounds of the halogens with H, and of the ternary compounds with H and O, brings out the resemblances and differences between the four elements. The compounds HX are all gases at ordinary temperatures; the formula HX expresses the composition of the molecules of each, but at low temperatures the V.D. of hydrogen fluoride is greater than that calculated from the formula HF. According to Thorpe and Hambly (*C. S. Trans.* 1888. 765; 1889. 163) there is no proof of the separate existence throughout any considerable temperature-interval of molecules heavier than those whose composition is expressed by the formula HF. Aqueous solutions of HX all contain acids; whether the acidic reactions of these solutions are the reactions of HX, or of a compound or compounds, $HX.nH_2O$, (? $H_2X.OH$), cannot be regarded as yet finally determined (*v.* vol. i. p. 534; ii. p. 8). The readiness with which stable acid fluorides, *e.g.* KF.HF, $BiF_3.3HF$, are formed, whereas corresponding chlorides, bromides, and iodides are few in number and unstable, points to the probable existence of H_2F_2 as the chemically reacting unit of hydrofluoric acid. The formation of these stable acid fluorides, and also of such definite acids as $SiF_4.2HF$ ($=H_2SiF_6$), $BF_3.HF$ ($=HBF_4$), $SnF_4.2HF$ ($=H_2SnF_6$), differentiates F from Cl, Br, and I. But it is to be noted that HCl, HBr, and HI combine with chlorides, bromides, and iodides of Hg, Au, and Pt, to form compounds which react as definite acids, *e.g.* H_2HgCl_4, H_2HgI_4, H_2PtBr_6, $HAuBr_4$. The heat of neutralisation of HFAq is 18 to 19 p.c. greater than that of the other acids, HXAq; on the other hand, the relative affinity of HFAq is very small, while HClAq, HBrAq, and HIAq are very strong acids (*cf.* Affinity, vol. i. p. 75).

According to the electrolytic dissociation-hypothesis of chemical change in solution (*v.* Physical methods), the small affinity of HFAq indicates that in solution only a few molecules HF (or ? H_2F_2) are dissociated into their ions; whereas most of the molecules HCl, HBr, and HI are dissociated in aqueous solutions of these compounds. If this is so, it is probable that the affinity of F for H is much greater than that of either Cl, Br, or I for H. The stability of the fluorides generally, and especially the stability of some non-metallic fluorides containing relatively much F, compared with the relatively unstable character of corresponding chlorides, bromides, and iodides, points to the affinity of F for metals and non-metals generally, as being greater than that of any of the other three halogen elements; *e.g.* compare PF_5 with PCl_5, or BiF_3 with $BiCl_3$.

Br decomposes most iodides with liberation of I; Cl decomposes both bromides and iodides with liberation of Br or I respectively; the reactions of F with chlorides, bromides, and iodides have not been yet examined.

The atoms of the halogens are monovalent in gaseous molecules. The gaseous molecules of Cl, Br, and I are diatomic; but the vapour-densities of bromine and iodine indicate the gradual dissociation of the diatomic molecules Br_2 and I_2 into the monatomic molecules Br and I as temperature increases. In the case of iodine dissociation is almost complete at about 1500°, but the lowest S.G. obtained for bromine (at c. 1570°) agrees approximately with that calculated for $\frac{2}{3}Br_2$. The results obtained with chlorine at c. 1500° indicate only a very slight dissociation of the diatomic molecule Cl_2. Experiments in this direction have not yet been made with fluorine. (For details *v.* Bromine, vol. i. p. 536; Chlorine, vol. ii. p. 11; and Iodine.) I dissolves in ether and some other solvents to form red solutions, and in CS_2, &c., to form violet solutions; Loeb's results (*C. S. Trans.* 1888. 805) indicate that the molecule of I in the red solutions is probably I_4, and that in the violet solutions the molecule is less complex than this; the values obtained were between I_3 and I_2.

The halogens show a gradation of prominent physical properties: F is a colourless gas, Cl is a yellowish-green gas easily condensed to a liquid, Br is a dark-red liquid with low B.P., and I is a lustrous greyish-violet solid.

None of the halogens combines directly with O. In their compounds with O and with O and H the halogens show considerable differences. No oxide of F or Br has yet been isolated; the oxides of Cl which certainly exist are Cl_2O and ClO_2; only one oxide of I, viz. I_2O_5, has been certainly isolated. The oxides of Cl are very unstable explosive gases; I_2O_5 is a stable well-defined solid. Cl_2O is the anhydride of hypochlorous acid HClO; ClO_2 reacts with water to form both chlorous and chloric acids $HClO_2$ and $HClO_3$; I_2O_5 is the anhydride of iodic acid HIO_3.

The oxyacids of Cl are HClO, $HClO_2$, $HClO_3$, and $HClO_4$; only the last has been obtained apart from water, the others are known in aqueous solutions only. The oxyacids of Br are HBrO and $HBrO_3$; neither is known otherwise than in aqueous solution. The oxyacids of I are HIO_3 and H_5IO_6; both have been isolated as solids. No oxyacid of F has yet been obtained. Solutions of the two acids HClO and HBrO are obtained by similar processes, viz. by reactions between HgO and ClAq or BrAq; when $Ba(ClO_3)_2$, $Ba(BrO_3)_2$ or $Ba(IO_3)_2$ is decomposed by the proper quantity of dilute H_2SO_4Aq, a solution of the corresponding acid, $HClO_3$, $HBrO_3$, or HIO_3, is obtained. Salts of these acids are also obtained by oxidising chlorides, bromides, or iodides; the conditions differ somewhat in each case (*v.* vol. i. p. 537; ii. p. 15; and Iodine, oxyacids of, in vol. iii.). The following thermal data regarding the formation of hydracids and oxyacids of the halogens are taken from Thomsen:—

	M=Cl	M=Br	M=I
[H,M] . .	22,000	8,440	−6,040
[H,M,Aq]. .	39,315	28,380	13,170
[H,M,O,Aq] .	29,930	26,080	—
[H,M,O^3,Aq] .	23,940	12,420	55,800

Thomsen also gives these data:—

[M^2,O,Aq] .	−8,490	−16,200	—
[HMAq,O^3] .	−15,380	−15,960	42,630

These numbers connect the differences between the relative stabilities of the acids of Cl, Br, and I, with differences between the quantities of energy degraded in their formations from their elements.

From Thomsen's thermal values we might fairly expect HIO_3 to be a more stable acid than $HClO_3$ or $HBrO_3$; we might also expect HIO_3Aq to be more readily produced by oxidising HIAq, than $HClO_3$Aq or $HBrO_3$Aq from a solution of the corresponding hydracid; and we might also expect HI or HIAq to be more unstable than the corresponding compounds of Cl or Br.

Chlorine water is an oxidising agent; but the oxidising action of bromine water is very small. Thomsen's thermal measurements connect these facts with energy-changes; he gives the following *constants of oxidation*:—

$$\text{(i)}\ 2[H,Cl,Aq]-[H^2,O]=10,270$$

$$\text{(ii)}\ 2[H,Br,Aq]-[H^2,O]=-11,600.$$

(i) represents the heat produced when chlorine decomposes water with formation of HClAq and O; (ii) represents the heat which disappears in the corresponding reaction of Br with water.

The heats of formation of Cl_2O and I_2O_5 are very different: $[Cl^2,O]=-17,930$; $[I^2,O^5]=45,030$ (Thomsen). If we compare the heats of formation of the oxyacids of Cl and Br with the heats of formation of the oxyacids of I, we see that the quantity of heat produced in the cases of Cl and Br decreases as the quantity of O increases, but increases in the case of I as the quantity of O increases (*v. supra*). The heat of formation of periodic acid H_5IO_6 is very much greater than that of any other oxyacid of I; Thomsen gives $[H^5,I,O^6,Aq]=184,400$, and $[HIAq,O^4]=34,510$.

Chlorine and iodine are the only halogens which form oxyacids higher than HMO_3; perchloric acid is $HClO_4$, but the only periodic acid which has been isolated is H_5IO_6. The composition of these two acids marks a point of difference between Cl and I. A great many periodates are known which have few if any analogues among the salts of Cl oxyacids. The periodates may be arranged in four classes:

meta-periodates, *e.g.* KIO_4, derived from the hypothetical acid HIO_4 $(=H_5IO_6-2H_2O)$;
meso-periodates, *e.g.* $Pb_3(IO_5)_2$, derived from the hypothetical acid H_3IO_5 $(=H_5IO_6-H_2O)$;
para-periodates, *e.g.* $Ba_5(IO_6)_2$, derived from the acid H_5IO_6;
di-periodates, *e.g.* $K_4I_2O_9$, derived from the hypothetical acid $H_4I_2O_9$ $(=2H_5IO_6-3H_2O)$.

(For details *v. Periodates*, under IODINE, OXYACIDS OF.)

The oxyacids of Cl and Br are all monobasic; but periodic acid H_5IO_6 is pentabasic, and iodic acid HIO_3 or $H_2I_2O_6$ is probably dibasic (*v.* IODINE, OXYACIDS OF).

The affinities of the hydracids of Cl, Br, and I are approximately equal; the affinity of HFAq is very small, less than $\frac{1}{100}$th of that of HClAq. The affinities of the oxyacids of the halogens, except that of $HClO_3$Aq, have not yet been determined; $HClO_3$Aq is nearly as strong an acid as HClAq. The data for comparing the increase in the affinity of an acid when H is substituted by F, Cl, Br, and I respectively are as yet very meagre; from the measurements which have been made the substitution of Cl seems to raise the affinity a little more than substitution of Br or F.

In the classification of the elements on the basis of the periodic law (*v.* vol. i. p. 351; also CLASSIFICATION, vol. ii. p. 203) the halogens are placed in Group VII., Cl, Br, and I in odd series, (3, 5, and 7), and F in an even series (2). Group VII. also contains Mn. The analogies between Mn and the halogens are but feebly marked. Physically, Mn is a metal; chemically it is both metallic and non-metallic. The permanganates M^IMnO_4 are generally isomorphous with the perchlorates, and with some of the meta-periodates. There are many gaps in Group VII.; at least four elements belonging to even series, and two belonging to odd series, have yet to be discovered. The position of Mn, following a series of metallic elements, and followed by the metals Fe, Ni, and Co, would lead us to expect pronounced metallic properties in this element. Looking generally at the variations of properties in groups and series, we should expect the analogy between Cl, which is the first member of the odd series of Group VII., and Mn, which belongs to the even series, to be but feebly marked; we should also expect to find the resemblances between the other even-series members of the group (when they are discovered) to be less distinctly marked than is the case in the lower groups, and we should expect to find all the odd-series members (Cl, Br, I, and two elements yet to be discovered) to resemble one another fairly closely.

For details about the individual halogens *v.* BROMINE, CHLORINE, FLUORINE, and IODINE.

M. M. P. M.

HALOGENS, BINARY COMPOUNDS OF THE. The four halogen elements form numerous binary compounds both with metals and non-metals. The compositions of the chief compounds in question are represented by general formulæ in the preceding article. Metallic fluorides, chlorides, bromides, and iodides may generally be prepared by dissolving metals or their oxides or carbonates in solutions of HF, HCl, HBr, or HI, and evaporating; many are also formed by the direct union of the elements; some are produced by reactions between metallic oxides or hydroxides, and Cl, Br, or I (probably a similar reaction will be found to occur with F). Metallic fluorides are not decomposed by heat alone; many of them are unchanged even when heated with carbon or oxygen; a few metallic chlorides are decomposed by heat alone to metal and Cl, *e.g.* $PdCl_4$; some are reduced by heat to lower chlorides, *e.g.* $CuCl_2$ to CuCl; but the majority are volatilisable without decomposition; metallic bromides and iodides as a class resemble chlorides in their behaviour towards heat; many chlorides, bromides, and iodides are decomposed with formation of oxy-haloid compounds or of oxides by strongly heating in moist air or oxygen. As a class, metallic chlorides, bromides, and iodides are soluble in water; some are decomposed to oxy-haloid salts; on the whole the iodides are less readily decomposed by water than the chlorides or bromides; metallic fluorides are generally insoluble in water; they are distinctly more stable towards water than the other haloid salts. Metallic fluorides very readily combine with HF to form acid salts, which are generally decomposed by heat with formation of the normal salt and HF. A few chlorides, bromides, and iodides combine with HCl, HBr, and HI respectively; but such acid chlorides are comparatively few in number, and are much less stable than the acid fluorides.

The non-metallic halogen binary compounds as a class are gasifiable; some, however, are decomposed by heat, *e.g.* chlorides and bromides of S; generally speaking the fluorides are more stable than the corresponding compounds of the other halogens. Most non-metallic chlorides and bromides are decomposed by water with formation of haloid acid and an oxyacid of the non-metal; in this respect iodides are more stable than chlorides and bromides, and fluorides are more stable than iodides.

Chlorine forms binary compounds with all non-metals except F; bromine with all except F, O, and perhaps N; iodine with all except B; and fluorine with all except Br, Cl, C, O, and N. The binary compounds of the halogens with H are acids, HCl, HBr, and HI are strong acids, but HF has a very small affinity. The binary compounds which the halogens form by combining one with another are not numerous; the chief are IF_5, ICl, ICl_3, IBr, BrCl; the only one of these which has been gasified without decomposition is ICl. M. M. P. M.

HALOID SALTS. Binary compounds of the halogens F, Cl, Br, I, with metals.

HAMATHIONIC ACID $C_{12}H_{18}SO_{16}$. An acid produced by the action of H_2SO_4 on euxanthic acid (Erdmann, *A.* 60, 240). Syrup; decomposed by boiling water.- $Pb_3C_{12}H_{12}SO_{16}$.

HARMALINE $C_{13}H_{14}N_2O$. *Harmine dihydride.* [c. 238°]. Occurs, together with harmine, in the seeds of *Perganum harmala*, a plant growing in Southern Russia. These alkaloids make up 4 p.c. of the seeds, and are found in the seed coating, not in the kernel (Göbel, *A.* 38, 363; Fritzsche, *A.* 64, 360; 68, 351, 355; 72, 306; 88, 327). Occur probably in the form of phosphates.

Preparation.—The seeds are extracted with dilute HOAc or H_2SO_4, and the brown extract mixed with NaCl. The hydrochlorides of the bases are ppd. together with colouring matter; the pp. is washed with brine, and then treated with pure water, which dissolves the hydrochlorides of the bases. The solution is treated with animal charcoal and the filtrate heated to 60° and mixed with ammonia. Harmine comes down first in minute needles, on further addition of ammonia harmaline is ppd. in minute scales.

Properties.—Trimetric octahedra (from alcohol); $a{:}b{:}c = 1{:}1{\cdot}804{:}1{\cdot}415$. Sl. sol. water and ether, m. sol. cold alcohol, v. sol. boiling alcohol. On oxidation with HNO_3 it forms harmine. Harmine is also formed when the acid chromate of harmaline is heated to 120°. By heating with HCl it is converted into harmalol.

Salts.—The salts of harmaline are yellow and exhibit strong fluorescence.—B'HCl 2aq: long yellow prismatic needles; m. sol. water and alcohol.—$B'_2H_2PtCl_6$: yellow pp.—$B'_2H_2Cr_2O_7$: crystalline.—**Acetate** is crystalline.—B'HCy: from harmaline hydrochloride and KCy. Formed also by dissolving harmaline in boiling dilute HCy. Thin tables (from alcohol). By heating to 180° or by boiling with water or alcohol it is resolved into harmaline and HCy. It combines with acids; thus HCl forms B'HCyHCl, a crystalline powder composed of small octahedra.

Methylo-iodide B'MeI. [260°] (O. Fischer a. Täuber, *B.* 18, 400).

Nitro-harmaline $C_{13}H_{13}(NO_2)N_2O$. [120°]. *Chrysoharmine.* Formed by suspending harmaline (1 pt.) in alcohol (7 pts. of 80 p.c.) adding conc. H_2SO_4 (2 pts.) and, when the solution is complete, moderately concentrated nitric acid (2 pts.); the mixture is heated to 100°, and when the reaction is over it is cooled quickly. The liquid then deposits the sulphate of nitro-harmaline, which is washed with alcohol containing H_2SO_4, dissolved in water, and treated with KOH. It may be further purified by sulphurous acid with which, unlike harmaline and harmine, it forms a sparingly soluble salt. Orange powder, composed of minute prisms (by ppn.); larger crystals are deposited from the alcoholic solution. Sl. sol. cold water, to which, however, it imparts a yellow colour; m. sol. boiling water; sl. sol. cold ether. More soluble in alcohol than harmine or harmaline. It expels NH_3 when heated with ammonium salts.

Salts.—B'HCl: small yellow prisms. — $B'_2H_2PtCl_6$: yellow pp., which ultimately assumes the form of minute prisms.—**Nitrate**: yellow needles; sl. sol. dilute HNO_3. — $C_{13}H_{12}Ag(NO_2)N_2O$ aq: yellowish-red flocculent pp., obtained by adding ammoniacal silver nitrate to a solution of nitro-harmaline nitrate.—**Normal sulphate**: crystalline pp.—$B'H_2SO_4$: pale-yellow crystalline powder, nearly insol. cold water.—B'HCy: obtained by dissolving nitro-harmaline in hot alcoholic HCy. Slender yellow needles. Resolved by boiling water into HCy and nitro-harmaline.

Harmine $C_{13}H_{12}N_2O$. [257°]. Occurs in the seeds of *Perganum harmala* (*v. supra*). Formed also by the oxidation of harmaline by a mixture of equal parts of alcohol and HClAq to which a little nitric acid has been added; the liquid is boiled, and on cooling harmine hydrochloride crystallises out in slender needles. The solution of this salt decomposed by NH_3 yields the base.

Properties. — Long colourless monoclinic prisms (from alcohol); nearly insol. water, less soluble in alcohol than harmaline, v. sl. sol. ether. Expels ammonia from boiling solutions of its salts. By heating with fuming HClAq at 140°, harmol and MeCl are formed (Fischer a. Tauber, *B.* 18, 400). CrO_3 oxidises it to harminic acid.

Salts.—Colourless; but in solution they exhibit indigo-blue fluorescence. - B'HCl 2aq: needles, sol. water and alcohol, v. sl. sol. HClAq. —B'HCl (from alcohol).—$B'_2H_2PtCl_6$: flocculent pp., becoming crystalline when the liquid is heated.—$B'_2H_2SO_4$ 2aq: concentrically grouped needles.—$B'H_2SO_4$ (from alcohol).—$B'_2H_2Cr_2O_7$. —$B'H_2C_2O_4$ aq: radiating needles.

Methylo-iodide B'MeI. [c. 298°]. Long white needles (F. a. T.).

Di-chloro-harmine $C_{13}H_{10}Cl_2N_2O$. Formed by heating a solution of harmine hydrochloride (2 pts.) in water (100 pts.) to boiling and adding conc. HClAq (15 pts.), followed by $KClO_3$ in small quantities until the brownish-red colour which at first appears is changed to pure yellow; on cooling, di-chloro-harmine hydrochloride separates and is washed with dilute HClAq. The salt is recrystallised from alcohol, and decomposed by boiling NaOHAq. Needles (from alcohol); insol. cold, v. sl. sol. boiling, water, sol. alcohol, ether, benzene, and CS_2. With iodine it forms a compound containing 46·5 p.c. iodine ($C_{13}H_{10}Cl_2N_2OI_2$ requires 47·5 p.c.).

Salts.—The salts of di-chloro-harmine are v. sl. sol. dilute acids; the normal salts are partially decomposed by much water, di-chloro-harmine separating. Ammonia ppts. the base from its salts as a jelly; NaOHAq also forms a gelatinous pp. which, however, becomes crystalline on long boiling with a large excess of NaOHAq.—B′HCl 2aq: needles (from water); separated from its aqueous solution by NaCl as a jelly which subsequently becomes crystalline. $B'HNO_3$: ppd. as a jelly, changing to needles, by adding HNO_3 to a solution of di-chloro-harmine in dilute HNO_3.

Nitro-harmine $C_{13}H_{11}(NO_2)N_2O$ (Fritzsche, *A.* 88, 328; 92, 330). Produced by the action of nitric acid on harmaline or nitro-harmaline. Prepared by dissolving harmaline (1 pt.) in water (2 pts.) and the requisite quantity of HOAc, and then adding HNO_3 (12 pts. of S.G. 1·40) in a thin stream. The liquid is boiled as long as nitrous fumes escape, and the nitro-harmine then ppd. by KOH. Yellow octahedra which soon change to needles (from alcohol); sl. sol. cold, m. sol. boiling, water. sl. sol. ether.—Hydrochloride: B′HCl 2aq: slender yellow needles. — Di-iodide $B'I_2$. Separates as minute yellowish-brown needles on mixing the boiling solutions of iodine and nitro-harmine in alcohol. In water, alcohol, and ether it is nearly insol. in the cold, but sl. sol. on warming. Boiling alcohol resolves it into iodine and nitro-harmine; boiling dilute H_2SO_4 acts in like manner.

Bromo-nitro-harmine $C_{13}H_{10}Br(NO_2)N_2O$. Ppd. by addition of bromine, followed by ammonia, to a dilute solution of a salt of nitro-harmine. When bromine-water is added to its solution in hot dilute alcohol there is deposited on cooling minute yellow needles of the dibromide $C_{13}H_{10}Br_4(NO_2)N_2O$.

Chloro-nitro-harmine $C_{13}H_{10}Cl(NO_2)N_2O$. Produced by the action of chlorine on nitro-harmine or of aqua regia on harmaline.

Preparation.—Harmaline (1 pt.) is dissolved in water (2 pts.), and the requisite quantity of HOAc, and the solution is poured into boiling nitric acid (12 pts. of S.G. 1·40) mixed with fuming HClAq (2 pts.). When the reaction is over a solution of NH_4Cl mixed with lumps of ice is poured into the liquid, which is afterwards further diluted, and ppd. by NaOHAq. Bright yellow brittle mass composed of minute needles. Ppd. from its salts by NH_3 as a jelly. Sl. sol. cold, m. sol. boiling water and boiling alcohol. Sl. sol. ether. Iodine solution forms slender needles of $C_{13}H_{10}Cl(NO_2)N_2OI_2$, sol. alcohol.

Salts.—B′HCl: slender, hair-like needles, m. sol. water. Ppd. from its aqueous solution by HClAq as a jelly, and by NaCl as white flocculi.—$B'_2H_2PtCl_6$: slender yellow prisms (from alcohol).

Harmine tetrabromide $C_{13}H_{12}N_2OBr_4$. Obtained as a reddish-yellow flocculent pp. on adding excess of bromine to a cold solution of harmine in dilute H_2SO_4 (O. Fischer, *B.* 22, 638). Reconverted into harmine by SO_2 or by warm aqueous Na_2CO_3.

Harmine tetrahydride $C_{13}H_{16}N_2O$.

Harmaline dihydride. [199°]. Obtained by reducing a hot concentrated solution of harmaline in alcohol by means of sodium (O. Fischer, *B.* 22, 638). Formed in the same way from harmine. Irregular pointed needles (from alcohol). Its solutions fluoresce pale bluish-green, becoming deep-green on addition of $FeCl_3$ or $AgNO_3$. Gives a nitrosamine $C_{13}H_{15}N_3O_2$.

Apoharmine $C_8H_8N_2$. [183°]. Got by distilling harminic acid (*v. infra*) in a partial vacuum in portions of ·5 g. at a time (O. Fischer, *B.* 22, 640).—$B'HAuCl_4$: yellow needles.—B′HI aq: fan-shaped groups of white needles (from MeOH), decomposing at 220° without melting.

Apoharmine tetrabromide $C_8H_8N_2Br_4$. A lemon-yellow pp. got by adding excess of bromine water to a solution of apoharmine in dilute H_2SO_4.

Apoharmine dihydride $C_8H_{10}N_2$. [49°]. (262°). Obtained by reducing apoharmine with conc. HIAq and red phosphorus at 160°. Tables (from ether-ligroïn). Smells of excrement of mice. From ether it separates with ether of crystallisation. Its solution in dilute H_2SO_4 exhibits violet fluorescence. Its hydrochloride colours pine-wood deep-orange.—B″HCl: felted needles. — $B''H_2PtCl_6$ 2aq: orange crystals. — $B''HAuCl_4$ [149°]: reddish-brown needles.

Nitrosamine $C_8H_9(NO)N_2$. [135°]. Small needles (from hot water). May be sublimed.

Harmol $C_{12}H_{10}N_2O$. [321°]. Formed by elimination of a methyl group from harmine $C_{13}H_{12}N_2O$, by heating it with fuming HCl at 140° (O. Fischer a. Täuber, *B.* 18, 402). Small needles. V. e. sol. aqueous alcohol, sl. sol. absolute alcohol, nearly insol. water. Dissolves in acids and in caustic alkalis. The acid solutions have a violet fluorescence.

Harminic acid $C_{10}H_8N_2O_4$. [345°]. Formed by oxidation of harmine in HOAc with CrO_3 (O. Fischer a. Täuber, *B.* 18, 403). Formed in like manner from harmaline. Silky needles, sl. sol. hot water, nearly insol. alcohol, ether, chloroform, and benzene. On heating to its melting-point it evolves CO_2, and yields apoharmine $C_8H_8N_2$ which melts at [183°].

Harmalol $C_{12}H_{12}N_2O$. Obtained as hydrochloride by heating harmaline (3 g.) with conc. HClAq (10 c.c.) at 150°. The base may be liberated by NaOH. Red needles, sol. hot water, sl. sol. benzene, sol. chloroform and acetone. Readily oxidised by air. It crystallises from dilute alcohol with 3aq.—B′HCl 2aq: crystals.—$B'_2H_2PtCl_6$.

Acetyl derivative $C_{12}H_{10}Ac_2N_2O$. Nodules.

Harmolic acid $C_{12}H_{10}N_2O_5$. [247°]. Formed by fusing harmol with KOH, and ppg. the aqueous solution of the melt with H_2SO_4. Small needles (from hot water). The solution of its ammonium salt gives amorphous pps., with salts of Pb, Cu, Ca, and Ag. On distilling in a partial vacuum harmolic acid yields a sublimate $C_{11}H_{10}N_2O$ in small needles, sl. sol. ether, m. sol. alcohol, forming a solution that fluoresces violet. This body appears to be a phenol and a base. It forms a platinochloride $B'_2H_2PtCl_6$ crystallising from hot water in small prisms united in stars, sl. sol. cold water, decomposing at about 180° (O. Fischer, *B.* 22, 642).

HARTIN $C_{10}H_{16}O$. *Psatyrin.* [210°]. (260°). A fossil resin resembling hartite. Crystallises from petroleum in triclinic needles. Sl.

sol. ether and boiling alcohol (Schrötter, *P.* 54, 45).

HARTITE $(C_6H_{10})_x$. [74°]. S.G. 1·05. A fossil resin found in Styria (Haidinger, *P.* 54, 261; Rumpf, *J. pr.* 107, 189). White triclinic crystals. V. sol. ether, m. sol. alcohol.

HATCHETIN. C. 86 p.c. H. 14 p.c. [46°]. S.G. $^{15·5}$ ·916. A transparent fossil resin found in the coal measures of Glamorganshire (Johnston, *P. M.* 12, 338). Sl. sol. boiling alcohol, m. sol. hot ether.

HEAT *v.* Physical methods, section *Thermal.*

HECDECANE *v.* Hexadecane.

HEDERIC ACID $C_{16}H_{26}O_4$. A substance occurring in the berries and leaves of the ivy (*Hedera helix*) (Posselt, *A.* 69, 62; Hartsen, *Ar. Ph.* April 1875; Davies, *Ph.* [3] 7, 275; 8, 205). Needles or delicate scales (Posselt). Davies found it to be uncrystallisable. V. sol. hot alcohol, v. sl. sol. ether, CS_2, chloroform, benzene, and water. Its solution does not redden litmus. Conc. H_2SO_4 colours it a splendid violet, the colour lasting some days; on pouring into water a flocculent greenish pp. is formed. According to Davies 'hederic acid' is not an acid. HNO_3 forms a nitro- derivative $C_{16}H_{25}(NO_2)O_4$, v. sol. chloroform. Block (*Ar. Ph.* [3] 26, 953) finds in ivy-leaves a glucoside $C_{32}H_{52}O_{10}$ 2aq.

HELENIN C_6H_8O. [110°]. Occurs in the root of elecampane (*Inula Helenium*), from which it may be extracted with hot alcohol (Gerhardt, *A.* 34, 192; 52, 389· *Gerh.* 4, 296; Kaller, *B.* 6, 1506). Needles, nearly insol. water, v. sol. alcohol. The crystals first obtained from the alcohol melt at 72°, being a mixture of helenin and inula-camphor [64°]; the latter is got rid of by repeated crystallisation from alcohol.

HELIANTHIC ACID $C_{14}H_{18}O_8$. An acid occurring in sunflower seeds (Ludwig a. Kromayer, *Ar. Ph.* [2] 99, 1, 285). Boiling dilute HCl splits it up into a fermentable sugar and an acid violet colouring matter.

HELIANTHIN *v. Di-methyl-amido-benzene-*azo*-benzene-sulphonic acid.*

HELICHRYSIN. A yellow pigment contained in the involucral bracts of *Helichrysum bracteatum* (Rosoll, *M.* 5, 94). Amorphous yellow mass, sl. sol. cold, v. sol. boiling, water, alcohol, and ether.

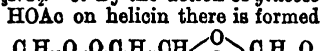
HELICIN $C_{13}H_{16}O_7$ *i.e.* $(C_6H_{11}O_5.O)C_6H_4CHO$. *Glucoside of o-oxy-benzoic aldehyde.* Mol. w. 284. [170°] (S.); [174°] (P.); [175°] (M.). $[\alpha]_D = -60·43$ in a 1·4 p.c. aqueous solution at 20° (Wegscheider, *B.* 18, 1600). S. 1·6 at 8°.

Formation.—1. By the action of very dilute HNO_3 upon salicin $(C_6H_{11}O_5.O)C_6H_4CH_2OH$ (Piria, *A. Ch.* [3] 14, 287; *B.* 14, 304; Sorokin, *J. pr.* [2] 37, 332).—2. By boiling its benzoyl derivative with magnesia (Piria, *A.* 96, 380).—3. By the action of acetochlorhydrose $C_6H_7ClAc_4O_5$ on potassium salicylic aldehyde, the substances being mixed in alcoholic solution and left for several days (Michael, *Am.* 1, 308; *C. R.* 89, 355).

Preparation.—Pulverised salicin (1 pt.) is mixed with nitric acid (10 pts. of S.G. 1·157) and the mixture left to itself; after 24 hours the salicin is dissolved and crystals of helicin have separated. They are washed with ether.

Properties.—Very slender, white silky needles (containing $\frac{3}{4}$aq). Neutral, slightly bitter, sl. sol. cold, v. sol. boiling, water, sol. alcohol, insol. ether. At 100° it gives off its water of crystallisation. Its solutions are lævorotatory. $FeCl_3$ gives no colouration. Conc. H_2SO_4 dissolves it with yellow colour. With $NaHSO_3$ helicin forms a hygroscopic crystalline mass of $C_{13}H_{16}O_7NaHSO_3$ (Schiff, *A.* 210, 126).

Reactions.—1. Under the influence of *emulsin* or of boiling dilute *acids* or *alkalis*, helicin is resolved into glucose and *o*-oxy-benzoic (salicylic) aldehyde.—2. *Sodium-amalgam* reduces helicin to salicin (Lesensko, *Z.* 1864, 577; *cf.* Swarts, *Institut.* 1865, 325).—3. When hot alcoholic solutions of helicin and *urea* are mixed together, and the liquid is allowed to evaporate, there is formed a thick syrup which, when kept over H_2SO_4, slowly solidifies. The product is the di-ureide $C_6H_{11}O_5.O.C_6H_4.CH(NH.CO.NH_2)_2$ and forms a hygroscopic crystalline powder, v. sol. water, forming a solution that is ppd. by $Hg_2(NO_3)_2$ but not by HNO_3 (H. Schiff, *G.* 12, 460). 4. An alcoholic solution of *thio-urea* forms $C_6H_{11}O_5.O.C_6H_4.CH(NH.CS.NH_2)_2$, a very hygroscopic crystalline powder (Schiff).—5. *Aniline* forms the anilide $C_6H_{11}O_5.O.C_6H_4.CH{:}NPh$, a yellow powder (containing aq), sol. alcohol and ether, insol. water. It is prepared by gently heating helicin with aniline, treating the product several times with acetic acid to remove excess of aniline, dissolving the residue in alcohol, adding ether, filtering, and ppg. with water (H. Schiff, *Z.* [2] 4, 638; *A.* 154, 31). By heating with aniline at 120° it is converted into the di-anilide $C_{25}H_{26}N_2O_5$. Both anilides are resolved by boiling dilute H_2SO_4 into glucose, helicin, and aniline.—6. *Tolylene-m-diamine* forms in like manner $(C_6H_{11}O_5.O.C_6H_4.CH{:}N)_2C_6H_3Me$, which crystallises in orange-red tufts; its solution exhibits marked green fluorescence.—7. By dissolving *m-amido-benzoic acid* in a cold aqueous solution of helicin a transparent vitreous mass is produced, which crystallises from alcohol in colourless plates [142°]. This compound is $C_6H_{11}O_5.O.C_6H_4.CH(OH).NH.C_6H_4.CO_2H$. On heating with acids it is split up into glucose, *m*-amido-benzoic acid, and salicylic aldehyde (H. Schiff, *G.* 10, 470).—8. *Amido-cuminic acid* forms in like manner the crystalline compound $C_{13}H_{16}O_7C_{10}H_{13}NO_2$.—9. By the action of *glucose* and excess of HOAc on helicin there is formed amorphous



$C_6H_{11}O_5.O.C_6H_4.CH\!<\!\begin{smallmatrix}O\\O\end{smallmatrix}\!>\!C_6H_{12}O_5$

(H. Schiff, *A.* 244, 26).—9. By adding *leucine* to an aqueous solution of helicin saturated with gaseous sulphurous acid there is formed $C_6H_{11}O_5.O.C_6H_4.CH(OH)SO_3NH_3.C_5H_{10}.CO_2H$, which crystallises with difficulty. Other amido-acids behave in like manner.—10. A solution of helicin (15 pts.) in water (500 pts.) heated to 55° and alternately treated with an aqueous solution of caustic soda (5 p.c. solution) and acetone (5 pts.) dissolved in water (40 pts.) deposits on cooling crystals of the glucoside of di-oxy-di-styryl ketone $(C_6H_{11}O_5.O.C_6H_4.CH{:}CH)_2CO$ [257°], while the filtrate on evaporation deposits the glucoside of oxy-di-styryl methyl ketone $C_6H_{11}O_5.O.C_6H_4.CH{:}CH.CO.CH_3$ [192°], of which the oxim melts at 178° (Tiemann a. Kees, *B.* 18, 1964).

Tetra-acetyl derivative $C_6H_7Ac_4O_5.O.C_6H_4.CHO$. Formed by mixing helicin with AcCl; after 24 hours the solution is heated to 60°, and the product extracted with ether and crystallised from alcohol (H. Schiff, *Z.* [2] 5, 1; *A.* 154, 22). Shining prisms; insol. water, sl. sol. ether and cold alcohol, v. e. sol. hot alcohol. Resolved by boiling dilute H_2SO_4 into glucose, HOAc, and salicylic aldehyde. With aniline at 80° it forms the anilide $C_6H_7Ac_4O_5.O.C_6H_4.CH{:}NPh$, a yellowish powder, sol. alcohol.

Benzoyl derivative $C_6H_{10}BzO_5.O.C_6H_4.CHO$. Obtained by dissolving populin (1 pt.) in nitric acid (11 pts. of S.G. 1·3). Formed also by treating helicin with BzCl. Tufts of silky needles; sl. sol. boiling water, m. sol. alcohol, insol. ether. Not attacked by emulsin, but boiling dilute acids and alkalis split it up into benzoic acid, glucose, and salicylic aldehyde. Boiling with water and magnesia resolves it into magnesium benzoate and helicin. Sodium-amalgam reduces it to populin $C_6H_{10}BzO_5.O.C_6H_4CH_2OH$. Aniline at 150° forms a brown resinous di-anilide $C_{32}H_{30}N_2O_6$.

Tetra-benzoyl derivative $C_6H_7Bz_4O_5.O.C_6H_4.CHO$. From helicin and BzCl at 160°. Amorphous. Sol. alcohol and ether, nearly insol. water. Aniline at 150° forms a brown resinous di-anilide $C_{53}H_{42}N_2O_9$.

Phenyl hydrazide $C_6H_4(OC_6H_{11}O_5).CH{:}N_2HC_6H_5$: [c. 187°]; white slightly crystalline solid. Sol. alcohol, ether, and hot water, nearly insol. cold water. By emulsin it is split up into glucose and salicylic aldehyde phenyl-hydrazide (Tiemann a. Kees, *B.* 18, 1657).

Oxim $C_6H_4(OC_6H_{11}O_5).CH{:}NOH$: [190°]; fine white needles containing aq. Sol. water, more sparingly sol. alcohol, insol. ether. By emulsin it is split up into glucose and salicylaldoxim. It is lævorotatory (Tiemann a. Kees, *B.* 18, 1662).

Bromo-helicin $C_{13}H_{15}BrO_7$ aq: gelatinous, drying up to an amorphous mass.

(α)-**Chloro-helicin** $C_{13}H_{15}ClO_7$. Obtained by agitating helicin with water in a vessel filled with chlorine. Small needles containing ½aq (from water). Sometimes it separates as an amorphous jelly. Nearly insol. cold, m. sol. hot, water; m. sol. alcohol. Emulsin or boiling dilute acids hydrolyse it, forming chloro-salicylic aldehyde and glucose.

(β)-**Chloro-helicin** $C_{13}H_{15}ClO_7$. A white granular substance obtained by passing chlorine into an alcoholic solution of helicin. Insol. water, nearly insol. boiling alcohol, not decomposed by emulsin, acids, or alkalis.

Isohelicin $C_{13}H_{16}O_7$. Formed by heating helicin to 185°. Formed also by moistening helicin with dilute (1 p.c.) nitric acid, leaving it for some days exposed to the air, and then heating to 110° (H. Schiff, *B.* 14, 318; *G.* 11, 112). Jelly; drying up to an amorphous powder. Decomposes at 250° without previous fusion. Sl. sol. water, alcohol, cold KOHAq, and HOAc. Boiling dilute H_2SO_4 slowly splits it up into glucose and salicylic aldehyde. By warming with very dilute HClAq it is changed into ordinary helicin.

Helicoidine $C_{26}H_{34}O_{14}$. This substance, which may be regarded as a compound of helicin with salicin, is obtained by treating salicin with very dilute nitric acid (S.G. 1·088) (Piria, *A. Ch.* [3] 14, 292). Needles containing 1¼aq (from boiling water). Split up by emulsin and by dilute alkalis into glucose, salicylic aldehyde, and saligenin. Aniline at 70° forms the amorphous di-anilide $C_{38}H_{44}N_2O_{12}$.

Octo-acetyl derivative $C_{26}H_{26}Ac_8O_{14}$. [80°]. From helicoidine and Ac_2O at 100° (H. Schiff, *A.* 154, 28). Drusic aggregates; insol. water, v. sol. alcohol and ether.

HELLEBORIN $C_{36}H_{42}O_6$. A glucoside that occurs sparingly in black hellebore (*Helleborus niger*) and more abundantly in green hellebore (*H. viridis*) (Husemann a. Marmé, *A.* 135, 55; *cf.* Weppen, *Ar. Ph.* [3] 2, 101, 193). Prepared by extracting old roots of green hellebore with alcohol, evaporating the extract, boiling the residue with water, and evaporating the aqueous extract till crystals are deposited on cooling. White, concentrically grouped needles (from alcohol), insol. cold water, sl. sol. ether, v. sol. boiling alcohol and chloroform. Decomposes when heated above 250°. Conc. H_2SO_4 colours it deep red, and then dissolves it with the same colour. Helleborin is a stronger narcotic than helleboreïn. It is resolved by boiling with dilute acids, or more completely with conc. $ZnCl_2Aq$, into glucose and helleboresin $C_{30}H_{38}O_4$. Helleboresin is a resinous body, insol. water, sl. sol. ether, v. sol. boiling alcohol; water separates it from its alcoholic solution as a flocculent pp.

Helleboreïn $C_{26}H_{44}O_{15}$. Occurs more abundantly in black than in green hellebore, but is present in greater quantity than helleborin even in the latter. The aqueous decoction of the root is ppd. with lead subacetate, the concentrated filtrate freed from excess of lead by sodium sulphate and phosphate, and the filtrate concentrated and ppd. with tannin. The pp. is stirred up with alcohol and PbO, dried, and exhausted with boiling alcohol; the helleboreïn is ppd. from the strongly concentrated alcoholic solution by ether. Transparent nodular groups of minute needles (from alcohol); on exposure to air these crumble to a yellowish-white hygroscopic powder. Helleboreïn has a sweetish taste, is v. e. sol. water, m. sol. alcohol, and insol. ether. It is poisonous. The aqueous solution, which scarcely reddens litmus, dries up to an amorphous mass which loses water at 120°, becomes straw-yellow at 160°, brown at 220°, and carbonises above 280°. Conc. H_2SO_4 dissolves it with brownish-red colour changing to violet. Alkalis and alkaline earths have no action upon it. Boiling dilute acids split it up into glucose and helleboretin. Helleboretin is deposited as a dark violet-blue pp. which, when dry, forms a grey-green amorphous powder, melting above 200°, insol. water and ether, sol. conc. H_2SO_4 forming a brownish-red solution whence it is ppd. by water in its original state. The alcoholic solution of helleboretin is red, and gives a brown colouration with H_2SO_4 (Greenish, *C. J.* 38, 719; *Ph.* [3] 10, 909, 1013). Helleboretin is not poisonous.

HEMELLITHENE *v.* HEMIMELLITHENE.

HEMELLITHENE-CARBOXYLIC ACID *v.* TRI-METHYL-BENZOIC ACID.

HEMELLITHENE SULPHONIC ACID *v.* TRI-METHYL-BENZENE-SULPHONIC ACID.

HEMI-ALBUMEN *v.* PROTEÏDS.

HEMI-COLLIN *v.* PROTEÏDS, *Appendix C.*

HEMIMELLITHENE $C_6H_3Me_3$ [1:2:3]. *c-Tri-methyl-benzene.* (175°). Formed by distilling (*a*)-cuminic acid with lime (O. Jacobsen, *B.* 15, 1857; 19, 2517). Formed also by the action of sodium upon a mixture of (2,1,3)-bromo-xylene and MeI (O. Jacobsen a. Deike, *B.* 20, 903).

Hemimellithene may also be isolated from coal-tar oil. It forms a tri-bromo-derivative $C_6Br_3Me_3$ [209°]. Coal-tar oil also contains another hydrocarbon boiling at 175° which yields a very soluble sulphamide [123°] and gives on oxidation two acids [121°] and [99°] (Jacobsen, *B.* 19, 2511).

HEMIMELLITHENOL $C_9H_{12}O$ *i.e.* $C_6H_2Me_3(OH)$[5:4:3:1]. [81°]. Formed by fusing the sulphonic acid of hemimellithene with potash (O. Jacobsen, *B.* 19, 2518). Long flat needles, sol. alcohol and ether. Not coloured by $FeCl_3$.

HEMIMELLITHIDINE *v.* CUMIDINE.

HEMIMELLITHYLIC ACID *v.* DI-METHYL-BENZOIC ACID.

HEMIMELLITIC ACID $C_9H_6O_6$ *i.e.* $C_6H_3(CO_2H)_3$[1:2:3]. *Hemimellithic acid. Benzene c-tri-carboxylic acid.* Mol. w. 210. [185°]. Formed, together with phthalic anhydride, by heating the hydride of mellophanic acid $C_6H_6(CO_2H)_4$ with H_2SO_4 (Baeyer, *A. Suppl.* 7, 31). Needles; begins to melt at 185°, being decomposed into phthalic anhydride, benzoic acid, CO_2, and H_2O. M. sol. cold water. Ppd. from its concentrated aqueous solution by HCl (difference from phthalic acid).—$Ba_3A'''_2$ 5aq: short thick needles, v. sol. water.—Ag_3A''': flocculent pp.

HEMI-PEPTONE *v.* PROTEÏDS.

HEMIPIC ACID $C_{10}H_{10}O_6$ *i.e.* $C_6H_2(OMe)_2(CO_2H)_2$[1:2:3or5:4]. *Di-methyl derivative of di-oxy-phthalic acid.* Mol. w. 226. [180°].

Formation.—1. By the oxidation of opianic acid $C_6H_2(OMe)_2(CHO)(CO_2H)$ by PbO_2 and H_2SO_4 (Wöhler, *A.* 50, 17), by aqueous $PtCl_4$ (Blyth, *A.* 50, 36, 43), or by chromic acid mixture (Matthiessen, *Pr.* 17, 341).—2. By the oxidation of narcotine by dilute HNO_3 (Anderson, *A.* 86, 194), by PbO_2 and H_2SO_4, by MnO_2 and H_2SO_4 (Wöhler; Liechti, *A. Suppl.* 7, 150), or by aqueous $PtCl_4$ (Blyth). In these reactions the narcotine is first converted into opianic acid.—3. Together with meconine $C_6H_2(OMe)_2<\substack{CH_2\\CO}>O$, by fusing opianic acid with potash (Matthiessen a. Foster, *Pr.* 11, 58; *C. J.* 15, 346; Beckett a. Wright, *C. J.* 29, 281).—4. By the oxidation of narceine.—5. By the oxidation of berberine (E. Schmidt, *B.* 16, 2589; Perkin, jun., *C. J.* 55, 71).—6. By the oxidation of papaverine by $KMnO_4$ (Goldschmiedt, *M.* 6, 380).—7. By boiling di-azo-hemipic acid (from amido-hemipic acid) with alcohol (Liebermann, *B.* 19, 2278; Grüne, *B.* 19, 2303).—8. Formed, together with cinchomeronic acid, by the action of 4 p.c. alkaline $KMnO_4$ on the di-methyl derivative of di-oxy-isoquinoline (Goldschmiedt, *M.* 9, 327).

Preparation.—Opianic acid is converted by hydroxylamine hydrochloride into opianic oxim anhydride which is then boiled with aqueous KOH. The product is acidified and the hemipic acid is extracted with ether (Goldschmiedt, *M.* 9, 765).

Properties.—Monoclinic efflorescent crystals (containing ½aq, aq, 2aq, or 2½aq). After drying at 100°, its melting-point varies from 157° to 175° according to the rapidity with which it is heated (G.). Sl. sol. cold water, m. sol. alcohol and ether. Its aqueous solution is acid in reaction. Sublimes in shining laminæ. Gives an orange colouration with $FeCl_3$. Gives the fluorescein reaction.

Reactions.—1. By boiling with HClAq or HIAq it is resolved into MeCl (or MeI) and the methyl derivative of di-oxy-phthalic acid (nor-hemipic acid) $C_6H_2(OH)(OMe)(CO_2H)_2$, which then splits up into CO_2, and the methyl derivative of protocatechuic acid (isovanillic acid) $C_6H_3(OMe)(OH)(CO_2H)$ [251°].—2. By heating with HClAq at 170° it is resolved into MeCl, protocatechuic acid and CO_2 (Wegscheider, *M.* 4, 270).—3. Heated with seven times its weight of KOH and a little water at 210° for fifteen minutes, it is converted into protocatechuic acid.—4. Distillation with *soda-lime* gives the di-methyl derivative of pyrocatechin (Beckett a. Wright).—5. Conc. H_2SO_4 converts it on heating into rufiopin (Liebermann a. Chojnacki, *A.* 162, 327).

Salts.—NH_4HA''aq. Needles.—KHA''½aq: large hexagonal tables, v. sol. water and alcohol, insol. ether.—Ag_2A'': white pp. insol. water.—Barium salt: when a solution of the barium salt is boiled, shining crystalline plates are deposited; the liquid on cooling redissolves this pp., but after standing for some hours, feathery tufts of very small silky needles separate; these dissolve on heating, and the crystalline plates are again deposited (Matthiessen a. Foster).—Ferric salt: orange-yellow pp.—Lead salt: white pp. insol. water, sol. $Pb(OAc)_2Aq$ whence it separates as transparent nodules.

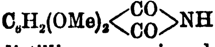
(*a*)-*Methyl ether* $C_6H_2(OMe)_2(CO_2Me)(CO_2H)$ [4:3or5:2:1]. [122°]. Formed by oxidising methyl opianate with aqueous $KMnO_4$ at 90° (Wegscheider, *M.* 3, 359). Long trimetric needles (containing aq or 1½ aq). Melts at 98° in its water of crystallisation. Sl. sol. cold, m. sol. hot, water, v. sol. alcohol, ether, and benzene, almost insol. ligroïn. Its aqueous solution is feebly acid in reaction, and gives a golden pp. with $FeCl_3$. On heating to 200° it gives hemipic anhydride. Distillation with lime gives the di-methyl- derivative of methyl protocatechuate, methyl-di-oxy-phthalic acid, hemipic acid, the methyl derivative of protocatechuic acid (isovanillic acid) and protocatechuic acid. By heating with conc. HClAq at 120° it is resolved into MeCl, hemipic acid $C_6H_2(OMe)(OH)(CO_2H)_2$, isovanillic acid $C_6H_3(OMe)(OH)(CO_2H)$ [4:3:1], and protocatechuic acid.

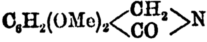
(*β*)-*Methyl ether* $C_6H_2(OMe)_2(CO_2Me)(CO_2H)$ [4:3or5:1:2]. [138°]. Formed by passing HCl into a solution of hemipic acid in MeOH (Wegscheider, *M.* 3, 359; *cf.* Anderson, *A.* 86, 195). Trimetric crystals (from chloroform); *a*:*b*:*c* = ·624:1:·758. V. sol. water, alcohol, ether, and benzene. Its aqueous solution gives no pp. with $FeCl_3$. At 200° it yields hemipic anhydride.

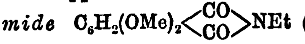
Ethyl ether $C_6H_2(OMe)_2(CO_2Et)(CO_2H)$. [132°] (A.); [142°] (W.). Formed by passing HCl into a solution of hemipic acid in alcohol. Needles (from MeOH) or monoclinic prisms (from benzene); v. sl. sol. cold, m. sol. hot, water; v. e. sol. MeOH, v. sol. alcohol and ether. Its aqueous solution is ppd. by $FeCl_3$.

Anhydride $C_{10}H_8O_5$. [167° cor.]. Formed by heating hemipic acid at 180° for an hour, and crystallising from alcohol (Beckett a. Wright, *C. J.* 29, 281). Formed also by treating hemipic acid with PCl_5 (Prinz, *J. pr.* [2] 24, 370). Shining needles. V. e. sol. hot benzene, v. sol. hot alcohol, m. sol. ether, insol. ligroïn. Reduced by boiling with zinc-dust and HOAc to pseudo-meconine. Boiling dilute alcoholic potash converts it into mono-ethyl hemipate (Matthiessen a. Wright, *Pr.* 17, 341).

Imide $C_{10}H_9NO_4$ *i.e.*


$C_6H_2(OMe)_2<\substack{CO\\CO}>NH$ (?). [230°]. Formed by distilling ammonium hemipate (Liebermann, *B.* 19, 2278). Formed also by molecular change from the isomeric compound opianic-oxim-anhydride by heating the latter to its melting-point [115°], heating it with conc. H_2SO_4, or with alcohol containing a trace of HCl. Hence it is produced in place of the oxim-anhydride by boiling opianic acid with an alcoholic solution of hydroxylamine hydrochloride (Liebermann, *B.* 19, 2923). Long slender colourless needles (from alcohol). The dilute alcoholic and aqueous solutions fluoresce blue. Sublimable. Dissolves in caustic alkalis but not in Na_2CO_3Aq. Hot KOHAq converts it into hemipic acid and NH_3. Boiling with tin and conc. HClAq converts it into 'hemipimidine' $C_{10}H_{11}NO_3$ or


$C_6H_2(OMe)_2<\substack{CH_2\\CO}>NH$ (?), [181°], which crystallises from benzene-ligroïn in laminæ and gives a nitrosamine $C_{10}H_{10}(NO)NO_3$ [156°], whence hot aqueous NaOHAq forms nitrogen and pseudo-meconine $C_{10}H_{10}O_4$ (Salomon, *B.* 20, 884).—$C_{10}H_8KNO_4$: crystalline solid.—$C_{10}H_8AgNO_4$: white pp.

Ethyl-imide 
$C_6H_2(OMe)_2<\substack{CO\\CO}>NEt$ (?). [98°]. Formed by heating the potassium derivative of the imide with EtI, or by distilling ethylamine hemipate. Needles (from water); v. e. sol. alcohol and ether (L.).

Iso-imide $C_{10}H_9NO_4$. [above 320°]. Formed, together with other bodies, by oxidising papaverine with $KMnO_4$ (Goldschmiedt, *M.* 8, 512). Small needles (from water). May be sublimed. V. sl. sol. hot water, alcohol, and ether, m. sol. hot HOAc. The alcoholic solution exhibits blue fluorescence. Boiling KOHAq splits it up into NH_3 and hemipic acid.

Ethyl-iso-imide $C_{10}H_8EtNO_4$. [227°]. Formed by oxidising papaverine ethylo-bromide with $KMnO_4$ (G.). Needles (from alcohol); sl. sol. boiling alcohol; sublimes in colourless needles. Potash converts it into ethyl-hemipamic acid $C_6H_2(OMe)_2(CO_2H)(CONHEt)$ which resembles the corresponding benzyl derivative.

Benzyl-iso-imide $C_{10}H_8(CH_2Ph)NO_4$. [225°]. Formed, together with other products, by oxidising papaverine benzylo-chloride (30 g.) with 2 p.c. aqueous $KMnO_4$ (100 g.) (Goldschmiedt, *M.* 9, 327). Needles (from alcohol). May be sublimed. Neutral; insol. dilute acids and alkalis. Split up by boiling KOHAq into hemipic acid and benzylamine, an intermediate product being the **mono-benzylamide** of hemipic acid $C_6H_2(OMe)_2(CO_2H)(CONHC_7H_7)$, which crystallises from alcohol in very slender needles, reconverted by heat into the imide. The mono-benzylamide is v. sol. aqueous alkalis; its K salt crystallises in needles, v. sol. water; its Ag salt is amorphous; the Ca salt, CaA'_2, crystallises in small needles, m. sol. water.

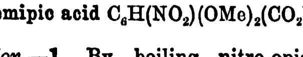
Nitro-hemipic acid $C_6H(NO_2)(OMe)_2(CO_2H)_2$. [166°].

Formation.—1. By boiling nitro-opianic acid with HNO_3 (4 pts.) (Liebermann, *B.* 19, 2285; Grüne, *B.* 19, 2303).—2. Together with nitro-pseudo-meconine, by heating meconine or pseudo-meconine (1 g.) with HNO_3 (10 c.c. of S.G. 1·14) for 1 hour at 150° (Salomon, *B.* 20, 888).

Preparation.—When opianic acid is nitrated by HNO_3 and the solid cake produced crystallised from water, nitro-opianic acid separates and nitro-hemipic acid remains in the mother liquor. Nitro-hemipic acid is obtained in larger quantity by heating opianic acid (50 g.) with HNO_3 (50 g.) as long as red fumes come off. The mass is crystallised from water and the mother liquor mixed with NH_3 and $BaCl_2$. Baric nitro-hemipate separates. The free acid is got by decomposing this with H_2SO_4 (Prinz, *J. pr.* [2] 24, 359).

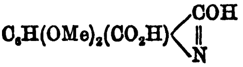
Properties.—Yellow prisms (containing aq).

Salts.—$A''K_2$: yellow prisms, v. sol. water and alcohol.—$A''Ag_2$: yellow pp.

Anhydride 
$C_6H(NO_2)(OMe)_2<\substack{CO\\CO}>O$: [145°]; thick yellow prisms; formed by heating the acid to 160°-165° (Liebermann, *B.* 19, 2285; Grüne, *B.* 19, 2303).

o-Amido-hemipic acid $C_{10}H_{11}O_6N$ *i.e.* $C_6H(OMe)_2(NH_2)(CO_2H)_2$. *Amido-di-methoxy-phthalic acid.* The free acid was not isolated as its solution easily decomposes on evaporation.

Formation.—1. By reduction of nitro-hemipic acid with $FeSO_4$ and NaOH.—2. By boiling the anhydro-acid (so-called 'azo-opianic acid')

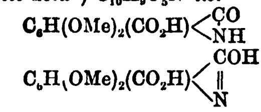

$C_6H(OMe)_2(CO_2H)<\substack{COH\\ \|\\ N}$ with excess of baryta-water.

Reaction.—By diazotisation and boiling with alcohol it may be converted into hemipic acid $C_6H_2(OMe)_2(CO_2H)_2$.

Salts.—$A''Na_2 3aq$: easily soluble long white needles.—$A''Ba$: glistening golden-yellow spangles, sl. sol. water.—$A''Cu 7aq$: slender green needles.—$A''Ag_2$*: yellowish-white pp. (Grüne, *B.* 19, 2301).

Acetyl derivative $C_6H(OMe)_2(NHAc)(CO_2H)_2$: [160°-170°]; colourless needles containing aq. Heated to 125° it is converted by elimination of water into the acetyl derivative of the anhydro-acid (Liebermann, *B.* 19, 2921).

Anhydro-*o*-amido-hemipic acid (so-called '*azo-opianic acid*') $C_{10}H_9O_5N$ *i.e.*



$$C_6H(OMe)_2(CO_2H){<}\begin{array}{l}CO\\ NH\end{array}$$

cr

$$C_6H(OMe)_2(CO_2H){<}\begin{array}{l}COH\\ \Vert\\ N\end{array}$$

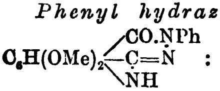
[200°]. Formed by boiling nitro-opianic acid with $SnCl_2$ and HCl (Prinz, *J. pr.* [2] 24, 364). Long white slender needles (from hot water). Decomposed on fusion. It dissolves in conc. H_2SO_4 and is thrown down unaltered by water. It is not affected by sodium-amalgam, or by $KMnO_4$ in presence of H_2SO_4. By boiling with baryta water it is converted into amido-hemipic acid $C_6H(OMe)_2(NH_2)(CO_2H)_2$ (Liebermann, *B.* 19, 2275 ; Grüne, *B.* 19, 2299).

Salts.—A'K: white crystalline powder.—A'Ag: white pp.—BaA'_2 6aq : slender needles.

Methyl ether A'Me : [127°].

Ethyl ether A'Et: [98°]; needles, sol. alcohol, ether, &c.

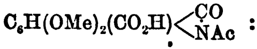
Phenyl hydrazide



$$C_6H(OMe)_2{<}\begin{array}{l}CO.NPh\\ C{=}N\\ NH\end{array}$$

: [222°] ; small glistening yellow tetragonal pyramids, $a:c = 1:0·5947$.

Acetyl derivative



$$C_6H(OMe)_2(CO_2H){<}\begin{array}{l}CO\\ NAc\end{array}$$

: [165°]; yellow needles. Formed by acetylation of the anhydro-acid; by heating amido-hemipic acid with Ac_2O and NaOAc ; or by heating acetyl-amido-hemipic acid to 125°. By warming with aqueous alkalis it is converted into acetyl-amido-hemipic acid (Liebermann, *B.* 19, 2920).

Propionyl derivative $C_{10}H_8(C_3H_5O)O_5N$: [139°].

Iso-hemipic acid $C_6H_2(OMe)_2(CO_2H)_2$[5:4:3:1]. [246°]. Formed by oxidising iso-opianic acid with a dilute solution of $KMnO_4$ (Tiemann a. Mendelsohn, *B.* 10, 398). White needles (from hot water) ; nearly insol. cold water, v. sol. alcohol and ether. May be sublimed. The salts of the alkalis and alkaline earths are easily soluble and crystallise well.

Mono-methyl ether MeHA''. [167°].

Nor-methyl-hemipic acid *v. Methyl derivative* of Di-oxy-phthalic acid.

Nor-methyl-nitro-hemipic acid *v. Methyl derivative* of Nitro-di-oxy-phthalic acid.

Nor-methyl-anhydro-amido-hemipic acid *v. Methyl derivative* of *Anhydro*-di-oxy-amido-phthalic acid.

HEMP. *Cannabis sativa.* Hemp-seeds contain about 25 p.c. of a drying oil, S.G. $\frac{15}{}$ ·928, which on saponification yields an acid $C_{18}H_{32}O_2$. When this acid is dissolved in HOAc and treated with bromine there is formed $C_{18}H_{32}Br_4O_2$ [115°] and $C_{18}H_{32}Br_6O_2$ [177°]. The acid $C_{18}H_{32}O_2$ yields on oxidation sativic acid $C_{18}H_{32}(OH)_4O_2$ (Hazura, *M.* 8, 147). Hemp leaves yield on distillation an essential oil $C_{15}H_{24}$ (257°), V.D. 7·1, S.G. $\frac{0}{0}$ ·93, $[\alpha]_D = -10·8°$ at 25·5° (Valente, *G.* 10, 479; 11, 196).

Indian Hemp *v.* Cannabis indica.

HENDECANAPHTHENE *v.* Hendecylene.

***n*-HENDECANE** $C_{11}H_{24}$. [−26·5°]. (195°). S.G. $\frac{0}{4}$ ·7559; $\frac{99}{4}$ ·6816. Formed by the action of HI and phosphorus at 230° upon hendecoic (undecylic) acid, or upon $C_{11}H_{22}Cl_2$ obtained by treating oil of rue with PCl_5 (Krafft, *B.* 15, 1697).

HENDECENOIC ACID $C_{11}H_{20}O_2$ *i.e.* $CH_2{:}CH(CH_2)_8.CO_2H$ (?). *Undecylenic acid.* [24·5°]. (165° at 15 mm.) (B.) ; (275° at 760 mm.) ; (199° at 90 mm.) (K.). Formed by distilling castor oil under diminished pressure (Krafft, *B.* 10, 2035 ; Brunner, *B.* 19, 2228). Large plates ; distils with decomposition at 275°. Split up by potash-fusion into acetic acid and *n*-ennoic acid $C_9H_{18}O_2$. Fuming HNO_3 oxidises it to sebacic acid $C_{10}H_{18}O_4$. With bromine it forms $C_{11}H_{20}Br_2O_2$ [38°]. HBr forms $C_{11}H_{21}BrO_2$ [35°]. HI gives $C_{11}H_{21}IO_2$ [24°].—BaA'_2 : flat needles or laminæ, S. ·093 at 15·5° (Becker, *B.* 11, 1412).

Di-hendecenoic acid $(C_{11}H_{20}O_2)_2$ *i.e.* $C_{10}H_{19}.CO.O.C_{10}H_{20}.CO_2H$. *Diundecylenic acid.* [30°]. (275° at 15 mm.). Formed, together with the following acid, by heating the preceding acid in a sealed tube above 300° (Krafft a. Becker, *B.* 10, 2034 ; 11, 1412 ; Krafft a. Brunner, *B.* 17, 2986). Formed also by the action of silver hendecenoate on iodo-hendecenoic acid (Brunner, *B.* 19, 2224). Crystallises from dilute alcohol. On heating with KOH hendecenoic acid is among the products. Br forms $C_{22}H_{40}Br_2O_4$, an almost colourless oil.

Poly-hendecenoic acid $(C_{11}H_{20}O_2)_x$. *Poly-undecylenic acid.* Formed as above, and also found in the residue after distilling castor oil. Amorphous. Gives ennoic acid on fusion with potash, and sebacic acid on treatment with HNO_3.

Hendecenoic acid $C_{11}H_{20}O_2$. *Petroleumic acid.* (250°–260°). S.G. $\frac{0}{}$ ·982 ; $\frac{23}{}$ ·969. Occurs in petroleum (Hell a. Medinger, *B.* 7, 1217 ; 10, 451 ; Markownikoff a. Ogloblin, *J. R.* 15, 345). Extracted from rectified petroleum by aqueous alkalis, and ppd. by H_2SO_4. Liquid. Not affected by potash-fusion or by nitrous acid. Does not combine with bromine. Boiling HNO_3 (S.G. 1·3) forms acetic acid and an acid $C_9H_{18}O_2$.—AgA': flocculent pp.

Methyl ether MeA'. (236°–240°) at 739 mm. S.G. $\frac{0}{}$ ·939 ; $\frac{27}{}$ ·919.

HENDECINENE $C_{11}H_{20}$. *Rutylidene.* (c. 200°) (Giesecke, *Z.* 1870, 431) ; (210°–215°) (Bruylants, *B.* 8, 413). Formed by the action of alcoholic KOH at 130° on $C_{11}H_{22}Cl_2$, obtained from $C_9H_{19}.CO.CH_3$ (in oil of rue) and PCl_5. Liquid. Gives a white pp. with ammoniacal $AgNO_3$ and a brownish-yellow pp. with ammoniacal Cu_2Cl_2.

HENDECINOIC ACID $C_{11}H_{18}O_2$. *Undecolic acid.* [59·5°]. From the dibromide of hendecenoic (undecylenic acid) $C_{11}H_{20}Br_2O_2$ and alcoholic KOH (Krafft, *B.* 11, 1414). Thin laminæ ; decomposed on distillation. V. sl. sol. water, v. sol. alcohol. Fuming HNO_3 oxidises it to arachic acid $C_9H_{16}O_4$.

Salts.—CaA'_2 aq.—BaA'_2. S. ·47 at 15·5°.—AgA'.

Hendecinoic acid $C_{11}H_{18}O_2$. (270°–280°). Among the products obtained by passing CO at 160° over a mixture of sodium isovalerate and sodium ethylate (Looss, *A.* 202, 321). Liquid.

HENDECOIC ACID $C_{11}H_{22}O_2$. *Undecylic acid.* [28·5°]. (228° at 160 mm.). Formed by heating hendecenoic acid (undecylenic acid) with HIAq and red phosphorus at 210°. Formed also by oxidising methyl hendecyl ketone $Me.CO.C_{11}H_{23}$ with chromic acid mixture (Krafft, *B.* 11, 2219; 12, 1667). Crystalline mass. Insol. water, v. e. sol. alcohol, sol. ether.—BaA'_2.—AgA'.

Hendecoic acid $C_{11}H_{22}O_2$ *i.e.* $(Me_3C)_2CMe.CO_2H$. *Methyl-di-tert-butyl-acetic acid.* [66°–70°]. (266° cor.). Formed by oxidising tri-iso-butylene with chromic acid mixture (Butlerow, *J. R.* 11, 203). Crystalline mass. Insol. water, v. e. sol. alcohol and ether.—$NaA'\frac{1}{2}aq$: crystalline. Absorbs CO_2 from the air, the acid being liberated.—**Magnesium salt**: v. sl. sol. cold water.

Methyl ether MeA'. (217°–220°).

Ethyl ether EtA'. (225°–230°).

Hendecoic acid $C_{11}H_{22}O_2$. *Umbellulic acid.* [c. 23°]. (275°–280° cor.). The glyceryl derivative of this acid constitutes the greater part of the fatty substance in the kernels of the Californian laurel (*Umbellularia californica*) (Stillman a. O'Neill, *Am.* 4, 206). Crystalline.—AgA'.

Methyl ether MeA'. (245°).

Ethyl ether EtA'. (254°).

Isoamyl ether $C_5H_{11}A'$. (295°).

HENDECONENE $C_{11}H_{18}$. (182°). Occurs, together with the following, in Dippel's animal oil (Weidel a. Ciamician, *B.* 13, 80). Does not combine with HCl.

Hendeconene $C_{11}H_{18}$. (203°). *V. supra.*

Hendeconene $(C_{11}H_{18})_x$. [196°]. Extracted by ether from *Cascara amarga* and *Phlox carolina* (Abbot, *B.* 21, 2598). Needles, sol. ether, HOAc, chloroform, hot alcohol, petroleum ether, and Ac_2O.

HENDECYL ALCOHOL $C_{11}H_{24}O$ *i.e.* $C_9H_{19}.CH(OH).CH_3$. (229°). S.G. ^{12} ·827. From oil of rue by reduction with sodium amalgam (Giesecke, *Z.* 1870, 428).

Hendecyl alcohol $C_{11}H_{24}O$. (245°–255°). A product of the action of sodium on isoamyl isovalerate (Lourenço a. Aguiar, *Z.* 1870, 404).

HENDECYL BROMIDE $C_{11}H_{23}Br$ *i.e.* $C_9H_{19}.CHMeBr$. From the corresponding alcohol (*v. supra*), Br, and P (Giesecke). Splits up on distillation into HBr and hendecylene $C_{11}H_{22}$.

HENDECYL CHLORIDE $C_{11}H_{23}Cl$. (220°–224°). Formed by chlorinating the hendecane in petroleum (Pelouze a. Cahours, *A. Ch.* [4] 1, 5).

HENDECYLENE $C_{11}H_{22}$. *Undecylene.* (193°). Formed by distilling hendecyl bromide (Giesecke).

Hendecylene $C_{11}H_{22}$. (195° cor.). S.G. ^{0} ·791. Occurs among the products of the distillation of the lime salts obtained by saponifying train oil (Warren a. Storer, *Z.* 1868, 230).

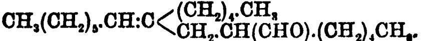
Hendecylene $C_{11}H_{22}$. (196° cor.). S.G. ^{0} ·840. Occurs in Burmese petroleum (W. a. S.).

Hendecylene $C_{11}H_{22}$. (194°). A product of the action of heat on paraffin (Thorpe a. Young, *A.* 165, 23).

Hendecylene $C_{11}H_{22}$. *Hendecanaphthene.* (180°). S.G. ^{0} ·812. Occurs in petroleum from Baku (Markownikoff a. Ogloblin, *J. R.* 15, 335). On chlorination it gives a mixture (210°–225°) of chlorides $C_{11}H_{21}Cl$, whence alcoholic KOH forms hydrocarbons $C_{11}H_{20}$, which combine directly with Br and H_2SO_4 but do not ppt. ammoniacal $AgNO_3$.

HENICOSANE $C_{21}H_{44}$. [40°]. (215° at 15 mm.). S.G. $\frac{40}{4}$ ·778; $\frac{99}{4}$ ·74. Formed by reduction of the dichloride $(C_{10}H_{21})_2CCl_2$ of the ketone $(C_{10}H_{21})_2CO$, obtained by the dry distillation of barium hendecenoate (Krafft, *B.* 15, 1718). Obtained also from brown coal paraffin by fractional distillation (Krafft, *B.* 21, 2263). Silvery plates.

HENICOSENOIC ALDEHYDE $C_{21}H_{40}O$ *i.e.*



$$CH_3(CH_2)_5.CH:C\begin{cases}(CH_2)_4.CH_3\\CH_2.CH(CHO).(CH_2)_4CH_3\end{cases}$$

Di-heptyl-heptoic aldehyde. (c. 320°) at 300 mm. S.G. $\frac{15}{15}$ ·874. Formed by the action of sodium amalgam on heptoic aldehyde; the yield being 5 to 10 p.c. (Perkin, jun., *C. J.* 43, 71). Slightly yellow oil; sol. CS_2. Reduces ammoniacal silver solution. Does not appear to combine with $NaHSO_3$. Combines with bromine (1 mol.) in CS_2. Decomposed by boiling with dilute H_2SO_4. Blackens when heated with potash.

***n*-HENTRIACONTANE** $C_{31}H_{64}$. [68°]. (302° at 15 mm.). S.G. $\frac{81}{4}$ ·773; $\frac{99}{4}$ ·762. Occurs in bee's wax (Schwalb, *A.* 235, 106). Formed by reduction of the dichloride $(C_{15}H_{31})_2CCl_2$ of palmitone $(C_{15}H_{31})_2CO$ with HI and P (Krafft, *B.* 15, 1714). Sl. sol. ether.

HEPTACOSANE *v.* Heptaicosane.

***n*-HEPTADECANE** $C_{17}H_{36}$. [23°]. (163° at 10 mm.); (223° at 100 mm.); (303° at 760 mm.). S.G. $\frac{25}{4}$ ·775; $\frac{30}{4}$ ·771; $\frac{100}{4}$ ·724. Hexagonal tables. Formed by reduction of the dichloride of methyl hexadecyl ketone, or of margaric acid with P and HI (Krafft, *B.* 15, 1702). Occurs in crystalline commercial scaly paraffin (Krafft, *B.* 21, 2256).

HEPTADECOIC ACID *v.* Margaric acid.

HEPTADECYLAMINE $C_{17}H_{35}NH_2$. [49°]. (335°–340°). Formed by distilling stearyl-heptadecyl-urea $C_{18}H_{35}O.NH.CO.NH.C_{17}H_{35}$ with lime (Hofmann, *B.* 15, 774; Turpin, *B.* 21, 2486). Fatty crystalline mass, sol. alcohol and ether. Absorbs moisture and CO_2 from the air. Not volatile with steam. Its ethereal solution evaporated with CS_2 forms $C_{17}H_{35}NH_3.S.CS.NHC_{17}H_{35}$ [90°], which on boiling with alcohol forms di-heptadecyl-thio-urea [94°]. The **hydrochloride** is insol. water, and crystallises from alcohol in plates with a fatty lustre.—$B'_2H_2PtCl_6$: minute yellow crystals.

Benzoyl derivative $C_{17}H_{35}NHBz$. [91°]. Crystallises from benzene in plates.

HEPTADECYL-CARBAMIC ETHER $C_{17}H_{35}NH.CO_2Et$. [62°]. Formed by the action of boiling alcohol on heptadecyl cyanate $C_{17}H_{35}N:CO$, an oil which is obtained by heating heptadecylamine hydrochloride with $COCl_2$ in benzene at 100° (Turpin, *B.* 21, 2486). Lustrous plates.

DI-HEPTADECYL KETONE $(C_{17}H_{35})_2CO$. [88°]. One of the products obtained by distilling stearyl-heptadecyl-urea with lime (Turpin, *B.* 21, 2487). Sl. sol. alcohol.

HEPTADECYL THIOCARBIMIDE $C_{17}H_{35}NCS$. [32°]. Formed, together with a small amount of di-heptadecyl-thio-urea, when heptadecylamine is heated with alcohol and CS_2 at 100° (Turpin, *B.* 21, 2486). V. sol. alcohol and ether. Cannot be distilled.

HEPTADECYL-THIO-UREA $C_{17}H_{35}NH.CS.NH_2$. [111°]. From the preceding and alcoholic NH_3 at 100° (T.). Sl. sol. alcohol.

Di-heptadecyl-thio-urea $(C_{17}H_{35}NH)_2CS$. [94°]. From heptadecylamine by boiling with alcoholic CS_2.

HEPTADECYL-UREA $C_{17}H_{35}NH.CO.NH_2$. [109°]. From heptadecylamine hydrochloride and alcoholic potassium cyanate (Turpin, *B.* 21, 2486). Sl. sol. alcohol.

Stearyl derivative $C_{17}H_{35}NH.CO.NH.C_{18}H_{35}O$. [112°]. Formed by the action of bromine and NaOH on the amide of stearic acid. Pearly laminæ (Hofmann, *B.* 15, 761).

Di-heptadecyl-urea $(C_{17}H_{35}NH)_2CO$. [73°]. From di-heptadecyl-thio-urea and HgO.

***n*-HEPTAICOSANE** $C_{27}H_{56}$. [60°]. (270° at 15 mm.). S.G. $\frac{60}{4}$ ·779; $\frac{100}{4}$ ·754. Formed by reduction of the dichloride of myristone $(C_{13}H_{27})_2CO$ with HI and P (Krafft, *B.* 15, 1713). Appears also to be present in bee's wax (Schwalb, *A.* 235, 106). Occurs also in commercial paraffin (Krafft, *B.* 21, 2264).

HEPTANAPHTHENE C_7H_{14}. (101°). A hydrocarbon in Caucasian petroleum (Milkowsky, *Bl.* [2] 45, 182).

***n*-HEPTANE** C_7H_{16} *i.e.* $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$. *Heptyl hydride. Methyl-hexane. Ethyl-amyl. Di-propyl-methane. Abietene.* Mol. w. 100. (98·43°) (Thorpe); (98·4° cor.) (Perkin, *C. J.* 45, 447). S.G. $\frac{0}{4}$ ·7005 (T.); $\frac{15}{15}$ ·6885; $\frac{25}{25}$ ·6814. M.M. 7·669 at 14·1°. C.E. (0°–10°) ·001222; (0°–100°) ·001439 (T.). H.C. 1137450 (Louguinine, *C. R.* 93, 274). S.V. 162·56 (T.); 165·0 (Ramsay). V.D. 50·0 (Theory 49·9). μ_D = 1·3879. R_D = 56·4 (calc. 55·8). *Coefficient of viscosity*: ·004236 at 15·3°. *Angle of capillarity* 167° (Thorpe). *Critical temperature*, 281° (Thorpe a. Rücker, *C. J.* 45, 165). Occurs almost absolutely pure in the exudation of the nut pine (*Pinus sabiniana*) (Thorpe, *C. J.* 35, 296; 37, 213; *cf.* Wenzell, *Ph.* [3] 2, 789). Occurs also in American petroleum, in coal-tar oil (Pelouze a. Cahours, *C. R.* 56, 505; Warren, *J.* 1865, 516; Schorlemmer, *C. J.* 15, 423; 26, 319; *Pr.* 14, 164, 464), and in Galician petroleum (Lachowicz, *A.* 220, 193). Formed by distilling azelaïc acid with baryta (Dale, *C. J.* 17, 258). Occurs, together with heptylene, amongst the hydrocarbons obtained by distilling the lime-soap of Menhaden oil (Warren a. Storer, *Z.* [2] 4, 231). Obtained also by distilling triolein under pressure (Engler, *B.* 22, 596). Treated with chlorine heptane gives a mixture of chloroheptanes (143°–158°). These may be converted into a mixture of a primary heptyl alcohol (165°–170°) and a secondary heptyl alcohol (156°–158°). By oxidising with chromic-mixture the former gives heptoic acid, the latter methyl amyl ketone and, by further oxidation, valeric and acetic acids; hence the alcohols are:

$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2OH$ and
$CH_3.CH_2.CH_2.CH_2.CH_2.CH(OH).CH_3$

(Schorlemmer a. Thorpe, *T.* 174, 270; *A.* 217, 150). The mixture of chlorides (143°–157·5°) is converted by alcoholic potash partly into heptylene (98·5°), partly into a mixture of ethyl heptyl oxides. The heptylene gives on oxidation valeric and acetic acids, hence it is $C_4H_9.CH:CH.CH_3$. Liquid bromine acting upon hot *n*-heptane forms chiefly secondary heptyl bromide; gaseous bromine forms primary and secondary heptyl bromides in about equal quantities. Liquid Br dissolved in cold heptane forms chiefly di-bromo-heptanes (Venable, *Am.* 10, 237).

Heptane $Me_2CH.CH_2.Et$. *Ethyl-isoamyl.* (90·35°) (Thorpe, *C. J.* 37, 216). S.G. $\frac{0}{4}$ ·69692 (T.); $\frac{18\cdot4}{}$ ·6833 (G.). C.E. (0°–10°) ·001253; (0°–50°) ·0013318; S.V. 161·98. V.D. 3·45 (calc. 3·47). A product of the distillation of whale oil under pressure (Engler, *B.* 22, 595). Formed by the action of sodium (14 pts.) on a mixture of EtI (60 pts.) and iso-amyl iodide (70 pts.) (Wurtz, *A. Ch.* [3] 44, 275). Formed also by gradually adding sodium to a mixture of ethyl and isoamyl bromides at 25°, then heating for a few hours at 100° and fractionally distilling (Grimshaw, *C. J.* 26, 309). Obtained also from $CH_3.CH(OH).CH_2.CH_2.CHMe$ by successive treatment with HI and with Zn and HCl (Purdie, *C. J.* 39, 467). According to Berthelot (*Bl.* [2] 9, 455) phthalic and terephthalic acid heated with (80 pts.) saturated HIAq yield a heptane (91°–93°); Berthelot also obtained by this treatment heptanes from toluene and from *o*- and *p*-toluidine (*C. R.* 68, 606).

Heptane CMeEtPrH. *Methyl-ethyl-propyl-methane.* (91°). S.G. $\frac{20}{20}$ ·6895. [α] + 2·70 for 100 mm. From active amyl iodide, propyl iodide and sodium (Just, *A.* 220, 153).

Heptane $CHEt_3$. *Tri-ethyl-methane.* (96°). V.D. 101·5. S.G. $\frac{27}{}$ ·689. Formed by the action of $ZnEt_2$ and sodium upon orthoformic ether (Ladenburg, *B.* 5, 752). Colourless liquid.

Heptane CMe_2Et_2. (87°). S.G. $\frac{0}{}$ ·7111; $\frac{20\cdot5}{}$ ·6958. Formed by the action of $ZnEt_2$ upon $CH_3.CCl_2.CH_3$ (from acetone), the distillate being mixed with water and fractionally distilled (Friedel a. Ladenburg, *A.* 142, 310). Besides *n*-heptane, Pennsylvanian petroleum contains a heptane (90°). S.G. $\frac{16}{}$ ·709 which is either CMe_2Et_2 or CHMeEtPr for it gives on oxidation a ketone $C_7H_{14}O$ (142°–146°) which on further oxidation yields nothing but acetic acid (Schorlemmer, *C. J.* 26, 319). The heptane in question gives rise to a mixture of heptyl chlorides (144°–158°), to a heptylene (90°–92°), to a primary heptyl alcohol (165°–170°), to a secondary heptyl alcohol (148°–150°), and to a heptoic acid (209°–213°).

References. — Di-bromo- and Di-chloro-heptane.

HEPTANE PHOSPHONIC ACID $C_6H_{13}CH_2PO(OH)_2$. [106°]. Formed by heating oxy-heptane phosphonic acid $C_6H_{13}CH(OH).PO(OH)_2$ with conc. HIAq at 200° (Fossek, *M.* 7, 29). Swells up in a little water, forming a jelly. Sol. alcohol, ether, and ligroïn.

Oxy-heptane phosphonic acid $C_6H_{13}.CH(OH)PO(OH)_2$. [185°]. From œnanthol by successive treatment with PCl_3 and water (Zepharovitch, *M.* 7, 28). Tables.

***n*-HEPTANE SULPHONIC ACID** $C_7H_{15}SO_3H$ (Winssinger, *Bull. Acad. Belg.* [3] 14, 12). Is converted by chlorine into a chloro- derivative of which the Ba salt is $(C_7H_{13}Cl_2SO_3)_2Ba$. A tri-chloro-sulphonic acid is also formed. ICl_3 yields two compounds, the one insoluble in water is $C_7H_8Cl_6O_3$ and the other is $C_7H_9Cl_5O_2$. The Ba salts of these acids crystallise out together forming crystals which on analysis correspond to the formula

$$2(C_7H_{12}Cl_3SO_3)_2Ba + 3(C_7H_8Cl_5O_2)_2Ba + 24aq$$

(Spring a. Winssinger, *Bl.* [2] 49, 68).

HEPTENE *v.* Heptylene.

HEPTENOIC ACID $C_7H_{12}O_2$. *Tetracrylic acid.* (218° i. V.). Formed by the dry distillation of turpenylic acid $C_8H_{12}O_4$ (Fittig a. Krafft, *A.* 208, 79). Liquid, smelling like valeric acid; lighter than water. Sl. sol. water. Gives acetic acid by potash-fusion. Combines with HBr forming $C_7H_{11}BrO_2$ which, on standing, changes to the anhydride of oxy-heptoic acid. Combines with bromine.—CaA'$_2$ 5aq: needles or prisms, v. sol. water.—AgA': small needles (from water).

Ethyl ether EtA'. (190°). (Amthor, ***Ar. Ph.*** [3] 18, 536).

Heptenoic acid Pr.CH_2.CH:CH.CO_2H. Formed by heating isovaleric aldehyde with HOAc and NaOAc (Fittig, *B.* 16, 1438). Liquid, volatile with steam.

Heptenoic acid Pr.CH:CH.CH_2.CO_2H. (225°). Formed, together with the lactone of oxy-heptoic acid, by heating propyl-paraconic acid (the lactone of oxy-butyl-succinic acid) (Fittig, *B.* 20, 3179).

Reference.—Chloro-heptenoic acid.

HEPTENYL BROMIDE $C_7H_{13}Br$. (165°). Formed by the action of alcoholic KOH on di-bromo-heptane derived from œnanthol and PBr_5 (Rubien, *A.* 142, 294; *B.* 8, 409).

HEPTENYL CHLORIDE $C_7H_{13}Cl$. *Chloro-œnanthylene. Chloro-heptylene.* (155° cor.). From di-chloro-heptane (œnanthylidene chloride) $C_7H_{14}Cl_2$ and alcoholic KOH (Limpricht, *A.* 103, 82). Heated with alcoholic KOH it yields C_7H_{12} which forms with alcoholic $AgNO_3$ a pp. $C_7H_{11}AgAgNO_3$ (Béhal, *Bl.* [2] 49, 581).

Heptenyl chloride $C_7H_{13}Cl$. (141°). From di-propyl ketone and PCl_5 (Tavildaroff, *B.* 9, 1442).

Heptenyl chloride $C_7H_{13}Cl$. (119°). S.G. ^{9} ·951. From di-isopropyl ketone and PCl_5 (Henry, *B.* 8, 400). Alcoholic KOH converts it into tetra-methyl-allylene (70°).

Heptenyl chloride $C_7H_{13}Cl$. (55° *in vacuo*). From the heptinene derived from perseite and HCl (Maquenne, *C. R.* 108, 101). Crystalline. Does not combine with **Br.** Potash reproduces the heptinene.

HEPTIC ACID (so called) $C_8H_{12}O_3$ (Pawloff, *C. R.* 97, 99); $C_7H_{10}O_2$ *i.e.* CH_3.CO.C(CO_2H):C_4H_8 (Demarçay). [151°]. One of the products of the action of alcoholic KOH on bromo-isobutyl-aceto-acetic ether (Demarçay, *C. R.* 86, 1135). Flat needles (from water); sol. chloroform, sl. sol. cold water. Colours $FeCl_3$ pale brown. Decomposes carbonates only on heating.

HEPTINENE C_7H_{12} *i.e.* Pr.CH_2.CH_2.C⁝CH. *Œnanthylidene. Heptine. Amyl-acetylene.* (107°) (R.); (102°) (B.). S.G. $\frac{0}{0}$ ·7508. Formed by boiling di-chloro-heptane Pr.CH_2.CH_2.CH_2.$CHCl_2$ with alcoholic KOH and heating the resulting heptenyl chloride with alcoholic KOH at 150° (Limpricht, *A.* 103, 84; Rubien, *A.* 142, 294). Oil, with alliaceous odour, lighter than water, v. sol. alcohol and ether. Bromine acts violently upon it, forming $C_7H_{12}Br_2$ and $C_7H_{12}Br_4$. Ammoniacal $AgNO_3$ gives a white pp.; ammoniacal Cu_2Cl_2 forms a yellow pp. (Bruylants, *B.* 8, 409). An alcoholic solution of $AgNO_3$ gives a pp. of $C_7H_{11}Ag_2NO_3$, sol. excess of the precipitant (Béhal, *Bl.* [2] 49, 335). When heated for 36 hours at 145° with alcoholic KOH in a sealed tube it changes to methyl-butyl-acetylene C_4H_9.C⁝CMe (Béhal, *A. Ch.* [6] 15, 428). When dissolved in excess of H_2SO_4 and distilled with water it gives methyl amyl ketone C_5H_{11}.CO.CH_3 (Béhal, *A. Ch.* [6] 15, 270).

Heptinene C_7H_{12}. (104°). S.G. $\frac{20}{0}$ ·803. From the product of distillation of rosin (Tilden, *B.* 13, 1605; Renard, *C. R.* 91, 419; Morris, *C. J.* 41, 173). Occurs also among the products of the action of boiling HIAq upon perseite (Maquenne, *C. R.* 107, 583; 108, 101). Liquid, not precipitated by ammoniacal $AgNO_3$.

Reactions.—1. Absorbs oxygen readily. Thus in 10 days it absorbs 100 volumes of oxygen, and if the product be distilled crystalline $C_7H_{14}O_2$ is got.—2. H_2SO_4 converts it into di-heptinene $C_{14}H_{24}$ (246°); V.D. 94·2.—3. HNO_3 (S.G. 1·3) forms a little *di-nitro-heptylene* $C_7H_{12}(NO_2)_2$ (*q. v.*), CO_2, formic, acetic, butyric, and succinic acids.—4. $K_2Cr_2O_7$ and H_2SO_4 give CO_2 and acetic acid.—5. Forms two bromides, $C_7H_{12}Br_2$ and $C_7H_{12}Br_4$.—6. When heated to a dull red heat it gives pentinene, hexinene (72°), benzene, toluene, and hydrogen, the two last named being the chief products (Renard, *C. R.* 104, 574).—7. Conc. HIAq forms, even in the cold, crystalline $C_7H_{13}I$. 8. Conc. HClAq at 150° forms crystalline $C_7H_{13}Cl$ which boils *in vacuo* at 55°.

Constitution.—MeCH:C:CHPr would give butyric and acetic acids on oxidation. Maquenne, however, considers the hydrocarbon to contain a tetra-methylene nucleus.

Heptinene C_7H_{12} *i.e.* CH_3.C⁝C.C_4H_9. *Methyl-butyl-acetylene.* (113°). S.G. $\frac{0}{0}$ ·763. Formed by heating C_5H_{11}.C⁝CH with alcoholic KOH at 150° (Béhal, *A. Ch.* [6] 15, 428). Liquid. Gives no pp. with ammoniacal Cu_2Cl_2, with ammoniacal $AgNO_3$, or with alcoholic $AgNO_3$. Gives a ketone on hydration. Forms a compound with $HgCl_2$.

Heptinene C_7H_{12} *i.e.* Et.C⁝C.C_3H_7. *Ethyl-propyl-acetylene.* (106°). S.G. $\frac{0}{0}$ ·760. Prepared from di-propyl ketone by treating with PCl_5, and heating the resulting $(C_3H_7)_2CCl_2$ with alcoholic KOH for 20 hours at 140° (Béhal, *Bl.* [2] 48, 216; *A. Ch.* [6] 15, 413). Liquid, with strong odour resembling acetylene. Does not react with ammoniacal Cu_2Cl_2. Forms a white compound with $HgCl_2$, which when treated with dilute HCl reproduces di-propyl ketone. Combines energetically with bromine. If the hydrocarbon be dissolved in conc. H_2SO_4, and the solution be diluted with ice, di-propyl ketone is obtained.

Heptinene C_7H_{12} *i.e.* Me_2C:C:CMe_2. *Tetra-methyl-isoallylene.* (70°). From di-isopropyl ketone by successive treatment with PCl_5 and alcoholic KOH (Henry, *B.* 8, 400). Does not ppt. ammoniacal $AgNO_3$ or Cu_2Cl_2.

Heptinene C_7H_{12}. *Heptylidene.* (115°-125°). Formed in small quantity in distilling calcium succinate (Funaro, *G.* 11, 276).

HEPTINENE GLYCOL *v.* Di-oxy-heptylene.

HEPTINOIC ACID $C_7H_{10}O_2$ *i.e.* Pr.CH_2.C⁝C.CO_2H. *Butyl-acetylene carboxylic acid.* (135° at 20 mm.). From methyl-propyl-acetylene (hexinene) by heating with sodium at 155° and treating the product, suspended in ether, with CO_2 (Favorsky, *J. R.* 1887, 553). Oil, which does not solidify at −20°. The silver salt soon decomposes into CO_2 and silver-hexinene.

Salts.—CaA'_2: slender needles (from water).—BaA'_2: small spangles (after drying over H_2SO_4).

HEPTINYL ALCOHOL $C_7H_{12}O$ *i.e.* $(CH_2{:}CH.CH_2)_2CH.OH$. *Di-allyl-carbinol.* (151° cor.). S.G. $\frac{0}{0}$ ·8758; $\frac{12}{0}$ ·8644. Formed by the action of zinc on a mixture of allyl iodide (2 vols.) and formic ether (1 vol.); the mixture is kept cold, and is finally mixed with water and distilled (Saytzeff, *A.* 185, 129; *B.* 9, 1600). A by-product in its preparation boils at c. 211°, and appears to be $C_{10}H_{18}O$, or di-allyl-carbinol, in which one H is displaced by propyl (W. Schestakoff, *J. pr.* [2] 30, 215). Di-allyl-carbinol is an oil. It unites with bromine, forming a tetrabromide. Chromic acid mixture oxidises it to formic acid and CO_2, no acetic acid being produced. $KMnO_4$ gives oxalic acid and an acid $C_5H_8O_3$ (Schirokoff, *J. pr.* [2] 23, 207). With HClO, followed by elimination of Cl, it gives, not $C_7H_{11}(OH)_5$, but its anhydride $C_7H_{11}(OH)_3O$ (S. Reformatsky, *J. pr.* [2] 31, 318).

Acetyl derivative $C_7H_{11}OAc$. (170° cor.). S.G. $\frac{0}{}$ ·9167; $\frac{17\cdot5}{0}$ ·8997 (Saytzeff, *A.* 185, 136).

Methyl ether $(C_3H_5)_2CH.OMe$. (136° i. V.). S.G. $\frac{0}{0}$ ·826; $\frac{20}{0}$ ·810. C.E. (0°–20°): ·001. Formed by the action of sodium and MeI on the alcohol (K. Rjabinin, *J. pr.* [2] 23, 270). *Reactions.*—1. When bromine is added to an ethereal solution combination takes place, a tetra-bromide, $(C_3H_5Br_2)_2CH(OMe)$, being formed.—2. Oxidised by $KMnO_4$, the double unions are broken, the product being the methyl derivative of β-oxy-glutaric acid $(CO_2H.CH_2)_2CH.OMe$ (*q. v.*).

Ethyl ether $(C_3H_5)_2CH.OEt$. (144° i. V.). S.G. $\frac{0}{0}$ ·821; $\frac{20}{0}$ ·802. C.E. (0°–20°) ·0012. From the alcohol by sodium and EtI (Rjabinin, *J. pr.* [2] 23, 272).

HEPTINYL CHLORIDE $C_7H_{11}Cl$ *i.e.* $(CH_2{:}CH.CH_2)_2CHCl$. (144°). From heptinyl alcohol and PCl_5. Converted by alcoholic KOH into heptonene C_7H_{10} (115°).

HEPTINYL GLYCOL *v.* DI-OXY-HEPTYLENE.

***n*-HEPTOIC ACID** $C_7H_{14}O_2$ *i.e.* $Pr.CH_2.CH_2.CH_2.CO_2H$. *Œnanthic acid.* Mol. w. 130. [–10·5°]. (223°); (222° cor.) (Perkin, *C. J.* 45, 484). S.G. $\frac{0}{0}$ ·9313 (Zander, *A.* 224, 69); $\frac{15}{15}$ ·9225; $\frac{25}{25}$ ·9160; $\frac{20}{4}$ ·9160 (Brühl). C.E. (0°–10°) ·00087. M.M. 7·552 at 14·5°. μ_β 1·4266 (B.). R_∞ 58·19. S.V. 174·6 (Z.).

Formation.—1. By the oxidation of œnanthol with nitric or chromic acid (Bussy, *J. Ph.* [3] 8, 329; *A.* 60, 248; Tilley, *A.* 67, 107; Schneider, *A.* 70, 112; Schorlemmer a. Grimshaw, *C. J.* 26, 1073; *A.* 170, 141; Mehlis, *A.* 185, 358).—2. By oxidation of castor oil (Tilley, *A.* 39, 160; *cf.* Arzbacher, *A.* 73, 200; Brazier a. Grossleth, *A.* 75, 249).—3. By the action of HNO_3 on oleic acid (Laurent a. Redtenbacher, *A.* 59, 50).—4. By saponification of hexyl cyanide, obtained from *n*-hexyl alcohol (Lieben a. Janecek, *A.* 187, 126).—5. By oxidation of *n*-heptyl alcohol (Schorlemmer, *Pr.* 14, 171; *A.* 161, 279; 170, 141).—6. By reducing isodulcite carboxylic acid with HI and phosphorus (E. Fischer, *B.* 21, 2175).—7. By the action of HNO_3 on Chinese wax (Buckton, *C. J.* 10, 166), on azelaic acid, and on spermaceti (Arppe, *A.* 120, 288).—8. By fusing sebacic acid with potash (Koch, *A.* 119, 173).—9. By boiling the barium salt of mannite carboxylic acid with aqueous HI and red phosphorus, diluting, and extracting with ether. The ethereal solution is shaken with mercury, and the product treated with H_2SO_4 and zinc-dust. The acid is finally distilled over with steam (E. Fischer a. Hirschberger, *B.* 22, 372).

Preparation.—Œnanthol (1 pt.) is treated in the cold with dilute HNO_3 (2 pts. composed of 1 vol. HNO_3 S.G. 1·4 and 2 vols. water); the resulting acid is distilled *in vacuo* (Krafft, *B.* 15, 1717).

Properties.—Liquid. Gives propionic and succinic acids when oxidised by chromic acid mixture.

Salts.—**Ammonium salt** is v. sol. water, alcohol, and ether, and non-crystalline.—KA' (at 100°): silky mass.—NaA': needles; often obtained as a jelly.—CaA'_2: thin flat needles. S. ·914 at 8·5° (S. a. G.).—CaA'_2aq: thin needles. S. (of CaA'_2) ·94 at 12° (L. a. J.).—BaA'_2: thin laminæ or broad needles. [239°] (M.). S. 1·76 at 12° (G. a. S.); 1·56 at 22° (M.); 1·68 at 9° (L. a. J.).—ZnA'_2: prisms (from alcohol); sl. sol. water, v. sol. alcohol. [132°].—$ZnA'_2\frac{1}{2}aq$.—CdA'_2: laminæ. [96°].—PbA'_2: laminæ (from hot water).—CuA'_2: green prisms (from alcohol).—AgA': small woolly needles (from hot water); insol. cold water and alcohol, sl. sol. boiling water.

Methyl ether MeA'. (180°) (Neuhof, *J.* 1866, 323); (173°) (Cahours a. Demarçay, *Bl.* [2] 34, 481); (172°) (Gartenmeister, *A.* 233, 249). S.G. $\frac{8}{}$ ·887 (N.); $\frac{18}{}$ ·889 (C. a. D.); $\frac{0}{0}$ ·8981 (G.). S.V. 196·2. C.E. (0°–10°) ·00102.

Ethyl ether EtA'. (188° i. V.). S.G. $\frac{0}{}$ ·8879 (L. a. J.); $\frac{0}{0}$ ·8861 (G.); $\frac{15}{15}$ ·8718; $\frac{25}{25}$ ·8648 (Perkin, *C. J.* 45, 502). M.M. 9·54 at 14·9°. C.E. (0°–10°) ·00101 (G.). By boiling the ether (20 c.c.) with *m*-amido-benzoic acid (10 g.) for eight hours there is formed $C_7H_{13}O.NH.C_6H_4.CO_2H$ [202°] (Pellizzari, *A.* 232, 149).

Propyl ether PrA'. (206·4°). S.G. $\frac{0}{0}$ ·8824. C.E. (0°–10°) ·0097. S.V. 246·5 (G.).

Butyl ether $PrCH_2A'$. (225·1°). S.G. $\frac{0}{0}$ ·8807. C.E. (0°–10°) ·00092. S.V. 271·3 (G.).

n-Heptyl ether $C_7H_{15}A'$. (274·6°) (G.); (277° cor.). S.G. $\frac{16}{}$ ·870 (Cross, *C. J.* 32, 123; *B.* 10, 1602); $\frac{15}{15}$ ·8652; $\frac{25}{25}$ ·8593 (Perkin); $\frac{0}{0}$ ·8761. C.E. (0°–10°) ·00086. S.V. 350·2. M.M. 14·655 at 13·6°.

Octyl ether $C_8H_{17}A'$. (290·4°). S.G. $\frac{0}{0}$ ·8757. S.V. 376·2. C.E. (0°–10°) ·0086 (Gartenmeister).

Phenyl ether C_6H_5A'. (275°–280°). From the chloride $C_7H_{13}OCl$ and phenol (Cahours, *C. R.* 39, 257).

Amide $C_6H_{13}.CONH_2$. [96°]. (250°–258°). Formed by heating the ammonium salt to 230° (Hofmann, *B.* 15, 983), and by the action of NH_3 on the anhydride (Mehlis, *A.* 185, 368). Laminæ (from water) or needles (from alcohol). Converted by a mixture of KOH and bromine into $C_6H_{13}NH.CO.NH.CO.C_6H_{13}$ [97°] (Hofmann, *B.* 15, 759).

Methyl-amide $C_6H_{13}CONHMe$. (266°). S.G. $\frac{15}{}$ ·895. Thick liquid. Obtained by heating the acid with methylamine for 5 hours at 230°, dissolving the product in ether, and adding K_2CO_3 (Franchimont a. Klobbie, *R. T. C.* 6, 247).

Di-methyl-amide $C_6H_{13}CONMe_2$. (243°). S.G. $\frac{15}{}$ ·894.

Ethylamide $C_6H_{13}.CO.NHEt$. [6°]. (268°).

Formed by heating the ethyl-ammonium salt at 230°. Decomposed by pure HNO_3 with evolution of N_2O (Franchimont a. Klobbie, *R. T. C.* 6, 248).

Di-ethyl-amide $C_6H_{13}.CO.NEt_2$. (258°). S.G. ^{15} ·881. Liquid (F. a. K.).

Anhydride $(C_6H_{13}.CO)_2O$. Mol. w. 242. (268°–271°). S.G. ^{21} ·932. Obtained by distilling the acid with PCl_5, and heating the resulting heptoyl chloride with potassium heptoate (Mehlis; *cf.* Chiozza a. Malerba, *A.* 91, 102).

Nitrile $C_6H_{13}.CN$. (175°–178° i. V.). S.G. ^{22} ·895. Formed by heating heptoic acid with potassium sulphocyanide (Mehlis). Formed also by the action of Ac_2O on the oxim of heptoic aldehyde (Lach, *B.* 17, 1572); and, together with heptylamine, by allowing a mixture of the amide of octoic acid (1 mol.) and bromine (3 mols.) to run into a 10 p.c. solution of NaOH (Hofmann, *B.* 17, 1407). Oil; sol. alcohol and ether.

Chloride $C_6H_{13}COCl$. With di-methyl-aniline in presence of $ZnCl_2$ it gives as condensation products, $C_6H_{13}.CO.C_6H_4NMe_2$, and a base $C_{23}H_{32}N_2$. This latter body has all the properties of a leuco-base. Heated with MeI at 100° it gives the salt $C_{23}H_{32}N_22MeI$. Oxidising agents act on it very easily, and develop a fine blue colour; Fe_2Cl_6 gives $C_{23}H_{30}N_2HCl$, having a fine blue colour. This is reduced by Zn in acid solution to the original leuco-base. The blue colour disappears with excess of acid. KOH or NaOH does not set free the base, but causes a complete decomposition (Auger, *Bl.* [2] 47, 48).

Isoheptoic acid $Pr.CH_2.CHMe.CO_2H$. *Methyl-butyl-acetic acid. Butyl-propionic acid.* (212°). S.G. $\frac{0}{0}$ ·9305; $\frac{21}{0}$ ·9138. S. ·36 at 4°. Formed by saponification of the corresponding nitrile which is obtained from KCy and the secondary hexyl iodide derived from mannite (Hecht, *A.* 209, 309; Hecht a. Munier, *B.* 11, 1781). Colourless oil; sl. sol. water, miscible with alcohol, ether and chloroform. On oxidation with chromic acid mixture it yields acetic and butyric acids. A solution of its Na salt gives white pps. with salts of Ca, Al, Zn, Cd, Mn, Hg, Pb, and Ag; a brown pp. with $FeCl_3$, a green pp. with $NiCl_2$, and a blue pp. with $CuSO_4$.

Salts.—KA′: very deliquescent, and v. e. sol. water.—NaA′: very deliquescent.—LiA′: crystalline, v. sol. water, m. sol. alcohol.—$CaA'_2 1\frac{1}{2}aq$: S. 11·9 at 1°; 13·9 at 6·7°; 12·1 at 16·8°; 11·3 at 28°; 6·1 at 100°.—$SrA'_2 2aq$: grouped needles. S. 19·2 at 3°.—$BaA'_2 1\frac{1}{2}aq$: crystalline aggregates. S. (of BaA'_2) 30 at 1°.—AgA′. S. ·23 at 4°.

Methyl ether MeA′. (157° i.V.). S.G. $\frac{15}{15}$ ·879.

Ethyl ether EtA′. (173° i.V.). S.G. $\frac{15}{15}$ ·8685; $\frac{27}{15}$ ·8570

Propyl ether PrA′. (192° i. V.). S.G. $\frac{19}{15}$ ·8635.

Isopropyl ether PrA′. (177°). S.G. $\frac{19}{15}$ ·859.

Heptoic acid $C_7H_{14}O_2$ *i.e.* $Pr.CH_2.CHMe.CO_2H$. (210° cor.). Formed from methyl-butyl-aceto-acetic ether and conc. alcoholic KOH. Formed from lævulose by shaking with HCy, decomposing the resulting $C_7H_{13}NO_6$ by fuming HClAq, and reducing the product with HI and phosphorus (Kiliani, *B.* 18, 3066; 19, 221). Oil.—$CaA'_2 6aq$: long needles. S. (of CaA'_2) 7·8 at 17·5°.—$SrA'_2 5aq$. This acid should be identical with the preceding, but does not seem to be so.

Heptoic acid $(CH_3)_2CH.CH_2.CH_2.CH_2.CO_2H$ (?) *Iso-amyl-acetic* or *iso-œnanthylic acid.* (216·5°–218° cor.). S.G. ^{15} ·926. Formed when CO is passed at 180° over NaOAc mixed with $NaOC_5H_{11}$ (Poetsch, *A.* 218, 67).

Salts.—NaA′aq.—$CaA'_2 3\frac{1}{2}aq$.

Methyl ether MeA′. (166°–167·5° cor.). S.G. ^{15} ·884.

Ethyl ether EtA′ (182° cor.). S.G. ^{15} ·872. Not attacked by alcoholic NH_3 at 120°.

Heptoic acid $C_7H_{14}O_2$. (210°–213°). Formed from isoheptane (ethyl-isoamyl) $Pr.CH_2.Pr$ by chlorinating, displacing Cl by OH, and oxidising the resulting heptyl alcohol (Grimshaw, *A.* 166, 168). Oil, with unpleasant odour. Probably identical with isoheptoic acid.—$CaA'_2 2aq$: small needles.—AgA′: small needles. The barium salt is amorphous.

Heptoic acid $(CH_3)_2CH.CH_2.CH_2.CH_2.CO_2H$. *Isoamyl-acetic acid.* An oil, formed by treating acetic ether with sodium and isoamyl iodide successively, the resulting isoamyl-aceto-acetic ether being saponified (Frankland a. Duppa, *A.* 138, 338). Probably identical with the acid of Poetsch.

Heptoic acid $C_7H_{14}O_2$. (209°–213°). Formed by oxidising the isoheptane (90°) in Pennsylvanian petroleum (Schorlemmer, *C. J.* 26, 319). Its barium salt is amorphous. The calcium salt crystallises by spontaneous evaporation in long transparent needles or prisms. The silver salt is a flocculent pp.

Heptoic acid $C_7H_{14}O_2$ *i.e.* $CH_3.CEt_2.CO_2H$. *Di-a-ethyl-propionic acid.* (208°). Formed by acting on $ZnEt_2$ with acetyl chloride; converting the resulting $CMeEt_2Cl$ into the corresponding iodide; heating this compound with KCy for a week; and digesting the resulting $CMeEt_2Cy$ with fuming HClAq (Idanoff, *Bl.* [2] 26, 450). Oil.—$BaA'_2 5aq$: separates on rapid cooling in stellate groups of flat needles; on slow cooling in flat prisms.—KA′: very soluble, and non-crystalline.—KHA'_2: stellate groups of needles.—The silver salt is sl. sol. boiling water, separating as tufts of small needles.—The lead salt is a white pp. sl. sol. cold water, the solution becoming turbid when heated.

Heptoic acid $C_7H_{14}O_2$ *i.e.* $(CH_3)_2CH.CHMe.CH_2.CO_2H$ (?). (220°). Formed by passing CO over a mixture of NaOEt and sodium isovalerate at 160° (Looss, *A.* 202, 321). Oil.

Heptoic acid $C_7H_{14}O_2$. *Amethenic acid.* (185°–230°). Obtained, together with CO_2 and acetic acid, by oxidising diamylene with K_2CrO_4 and dilute H_2SO_4 (Von Schneider, *A.* 157, 185). Oil, lighter than water. Its salts are decomposed even by CO_2. The K, NH_4, Ca, and Mg salts are crystallisable and v. sol. water.—$SrA'_2 8aq$: small needles (Wyschnegradsky a. Pawloff, *J. R.* 7, 170).—ZnA'_2: nodules, sl sol. cold water; the aqueous solution deposits a gelatinous pp. when heated.—AgA′: pulverulent pp., sl. sol. water.

Heptoic acid $CH_3.CH_2.CH_2.CHEt.CO_2H$. *Ethyl-propyl-acetic acid.* (209° cor.). From ethyl-propyl-aceto-acetic ether by saponification with conc. alcoholic KOH (Kiliani, *B.* 19, 227). Oil.—$CaA'_2 2aq$: soft needles. S. (of CaA'_2) 11·4 at 19·5°.—$SrA'_2 2aq$: small prisms. S. (of SrA'_2) 27·9.—$PbA'_2 3aq$.—CuA'_2. The silver, barium, and lead salts form colourless needles. The acid is perhaps identical with that of Hecht.

References.—Amido-, and Bromo-, HEPTOIC ACIDS.

HEPTOIC ALDEHYDE $C_7H_{14}O$ *i.e.* $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CHO$. *Œnanthol.* Mol. w. 114. (155°). S.G. $\frac{20}{4}$ ·8495 (Brühl); $\frac{15}{15}$ ·8226; $\frac{25}{25}$ ·8158 (Perkin, *C. J.* 45, 477). V.D. 4·14 (calc. 3·95). μ_β 1·4309. R_∞ 55·59. M.M. 7·422 at 16·2°. The name œnanthol is due to the belief of Liebig that heptoic acid was the chief product of the saponification of fusel oil from wine (Liebig a. Pelouze, *A.* 19, 241). Obtained by distilling castor oil (Bussy, *A.* 60, 246; *J. Ph.* 13, 62; [3] 8, 321; H. Schiff, *Z.* 1870, 77; Krafft, *B.* 10, 2035). Purified by preparing its compound with $NaHSO_3$, which is subsequently distilled with Na_2CO_3 (Bertagnini, *A.* 85, 281). Dried over Na_2SO_4 and rectified (Erlenmeyer a. Sigel, *A.* 176, 342). The yield is 12 p.c. of the castor oil (Jourdan, *A.* 200, 102). Oil, miscible with alcohol and ether. Has a strong odour. When moist heptoic aldehyde is exposed for a long time to a low temperature it deposits crystals of a hydrate $C_7H_{14}O\,\frac{1}{2}aq$ (? heptoic orthaldehyde) (Bouis, *A. Ch.* 44, 87). Heptoic aldehyde reduces $AgNO_3$, forming a mirror.

Reactions.—1. Heptoic aldehyde is polymerised by prolonged contact with K_2CO_3. The product is a crystalline solid [53°] which, when heated, begins to decompose at 115° into heptoic aldehyde, the aldehyde $C_{13}H_{25}CHO$, and an aldehyde $C_{28}H_{54}O_3$ (c. 335° at 250 mm.). The solid polymeride when treated in acetic acid solution with sodium yields heptyl alcohol and a substance $C_{21}H_{44}O_2$ (Bruylants, *L.* 8, 414; Perkin, jun., *C. J.* 43, 67).—2. Alcoholic (1·5 p.c.) potash yields tetradecenoic (amyl-hexyl-acrylic) acid $C_{14}H_{26}O_2$, its aldehyde $C_{14}H_{26}O$, the aldehyde $C_{28}H_{50}O$, and heptoic acid (Perkin, jun., *C. J.* 43, 67; *B.* 15, 2806).—3. Conc. KOHAq also forms condensation products, together with heptoic acid. 4. Solid KOH polymerises heptoic aldehyde even at 0°, forming a solid and a liquid polymeride. Each of these bodies when distilled gives heptoic aldehyde, tetradecenoic aldehyde, and $C_{28}H_{54}O_3$ (Borodin, *B.* 5, 481; 6, 982). Solid KOH at 120° forms an oil $C_{14}H_{28}O$ which boils, with decomposition, at 260° (Tilley, *P. M.* 33, 81; *A.* 67, 109).—5. $ZnCl_2$ forms the aldehyde $C_{14}H_{16}O$. 6. Cold conc. HNO_3 forms a solid isomeride 'metœnanthol.'—7. Dilute chromic acid mixture forms heptoic acid.—8. When left for some weeks in contact with quicklime, there is formed heptyl alcohol, heptoic acid, heptylene (95°–100°), octylene (122°–125°), ennylene (145°), and the ketone $C_{13}H_{26}O$ (Fittig, *A.* 117, 76).—9. In acetic acid solution *sodium* reduces it, forming heptyl alcohol, tetradecenyl alcohol $C_{13}H_{25}CH_2OH$, and tetradecenoic aldehyde $C_{13}H_{25}CHO$ (Perkin). In a wet ethereal solution Na forms heptyl alcohol, heptoic acid, tetradecenoic aldehyde, and a body $C_{21}H_{40}O$.—10. PCl_5 forms di-chloro-heptane $C_6H_{13}CHCl_2$.—11. PCl_3Br_2 forms $C_6H_{13}CHBr_2$. *Chlorine* forms oily $C_7H_{11}Cl_3O$ (A. W. Williamson, *A.* 61, 44).—12. *Resorcin* and dilute HCl form a resin in the cold (Michael a. Ryder, *Am.* 9, 134). 13. Heptoic aldehyde (20 g.) heated with trimethylene glycol (30 g.) at 160° gives rise to $C_6H_{13}.CH{<}\substack{O.CH_2\\O.CH_2}{>}CH_2$, an oil, (c. 216°), S.G. $\underline{0}$ ·933. With *glycol*, in like manner, it forms $C_6H_{13}.CH{<}\substack{O.CH_2\\O.CH_2}{>}$ (Lochert, *A. Ch.* [6] 16, 35, 52).—14. NaOAc and Ac_2O at 170° give ennenoic acid (Schneegans, *A.* 227, 85).—15. Ac_2O and barium succinate give hexyl-paraconic acid (Schneegans).—16. *Aqueous ammonia* (150 g. of S.G. ·89) added to cooled heptoic aldehyde (80 g.) forms an oily layer of heptoic aldehyde ammonia $C_6H_{13}.CH(OH)NH_2$ (Erlenmeyer a. Sigel, *A.* 176, 343).—17. *Dry ammonia* passed into dry heptoic aldehyde forms heptoic hydramide $(C_6H_{13}CH)_3N_2$, which boils above 400° and does not combine with acids. The hydramide is converted by boiling water into a yellow oil $C_{21}H_{11}NO$, and by water at 125° into $C_{28}H_{53}NO$, which is also a yellow neutral oil (Schiff, *A. Suppl.* 3, 367; *Suppl.* 6, 24).—18. Colourless *ammonium sulphide* in concentrated solution forms heptoic thialdine $C_{21}H_{43}NS_2$, a colourless oil, S.G. ^{24} ·896. It forms a hydrochloride B'HCl, which is insol. water, and crystallises from alcohol in needles (Schiff).—19. A solution of heptoic aldehyde saturated with *ammonia* is converted by *hydrogen cyanide* into oily $C_6H_{13}CH(NH_2).CN$, and another oil $C_{16}H_{29}N_3$ (Erlenmeyer a. Sigel, *A.* 177, 111).—20. If heptoic aldehyde (100 pts.) be mixed with a little PCl_5 (1 pt.) and dry *hydrogen sulphide* be passed in, there is formed the compound $C_6H_{13}.CH{<}\substack{O\\S}{>}CH.C_6H_{13}$, (200°–250°). S.G. $\underline{22}$ ·875 (Schiff).—21. An alcoholic solution of heptoic aldehyde, on saturation with HCl, yields $C_6H_{13}CHCl(OEt)$, a light oil, which is decomposed on distillation into a mixture of hydrocarbons and other bodies (Williamson; Schiff, *Z.* [2] 6, 74).—22. *Phosphonium iodide* at 0° forms $(C_6H_{13}.CH.OH)_4PI$, which crystallises in minute leaflets, [122°], insol. water, sl. sol. ether, v. sol. alcohol (Girard, *A. Ch.* [6] 2, 40).—23. *Isoamylamine* forms $C_6H_{13}.CH{:}NC_5H_{11}$, a yellow, non-volatile, basic oil (Schiff, *A.* 140, 93).—24. Heptoic aldehyde (70 g.) heated with *aniline* (57 g.) and HOAc (150 g.) at 100° forms $C_6H_{13}.CH(OH).NHPh$, a red oil with pleasant odour (Leeds, *A. C. J.* 5, 2).—25. By heating with *aniline* or di-phenyl-urea there is formed $C_6H_{13}.CH{:}NPh$ (or $(C_6H_{13}.CH)_2(NPh)_2$), a neutral yellow oil, which combines with isoamyl iodide at 100° forming $C_{26}H_{38}N_2C_5H_{11}I$ (Schiff, *A.* 148, 336; *Suppl.* 3, 351).—26. *Benzoyl-aniline* forms $C_6H_{13}.CH(NPhBz)_2$, which is split up on distillation into Bz_2O and $(C_6H_{13}.CH)_2(NPh)_2$ (Schiff). 27. *Ethyl-aniline* forms $C_6H_{13}.CH(NPhEt)_2$ (215°–220°), a neutral oil.—28. *Allyl-aniline* forms $C_6H_{13}.CH(NPhC_3H_5)_2$, a neutral oil.—29. *Di-phenyl-thio-urea* in the cold forms $C_6H_{13}.CH{<}\substack{NPh\\NPh}{>}CS$, a neutral solid, sol. ether (Schiff).—30. *Xylidine* in glacial acetic acid forms, according to Leeds (*A. C. J.* 5, 2), a red liquid $C_6H_{13}.CH(OH).NHC_6H_3Me_2$ with pleasant odour. 31. (*a*)-*Naphthylamine* in HOAc forms in like manner $C_6H_{13}.CH(OH).NHC_{10}H_7$, a red liquid.

smelling like pine-apples (Leeds).—**32.** (α)-*Naphthylamine* added to a dry ethereal solution of heptoic aldehyde forms a yellow, amorphous, neutral substance $(C_6H_{13}.CH)_2(NC_{10}H_7)_2$; insol. water, sol. alcohol and ether (Papasogli, *A.* 171, 139).—**33.** Treated with *di-methyl-aniline* in presence of $ZnCl_2$ there is formed (together with products resulting from the polymerisation of the aldehyde) a condensation product $C_{23}H_{34}N_2$ or $C_6H_{13}.CH(C_6H_4NMe_2)_2$. This forms long colourless needles [59·5°], (275° at 15 mm.); sl. sol. cold alcohol, insol. water. On oxidation this base does not yield the corresponding carbinol, but gives a passing colouration and an odour of œnanthol (Auger, *Bl.* [2] 47, 42).—**34.** $ZnEt_2$ followed by water forms the alcohol $C_6H_{13}.CHEt.OH$ (195°) (Wagner, *B.* 17, Ref., 315, Ref.).—**35.** Heptoic aldehyde (75 g.) heated with *aniline* (20 g.) and conc. HClAq (60 g.) for 2 hours at 100° forms amyl-hexyl-quinoline (Dœbner a. Miller, *B.* 17, 1719).

Combinations with sulphites.—The combinations with bisulphites of the alkalis may be obtained directly, or by passing SO_2 into an alcoholic solution of heptoic aldehyde containing potash, soda, or NH_3.—$C_6H_{13}.CH(OH).SO_3Na$ aq: brilliant unctuous scales; v. sol. water, v. e. sol. hot, nearly insol. cold, alcohol. Decomposed by acids and alkalis, with liberation of heptoic aldehyde. With $BaCl_2$ its solution gives a pp. of $(C_7H_{13}SO_3)_2Ba$, whence H_2SO_4 liberates oily $C_7H_{14}SO_3$, a compound which is also formed by passing SO_2 into an aqueous solution of heptoic aldehyde (Mendelejeff, *A.* 110, 241). — $C_7H_{13}SO_3NH_4$: small shining prisms, sl. sol. water and alcohol. Decomposed by boiling water into heptoic aldehyde and acid ammonium sulphite. When heated with potash-lime at 265° it yields tri-hexyl-amine (Petersen a. Gossmann, *C. C.* 1857, 193).—$(C_7H_{14}O)_2SO_2(NH_2Ph)_2$: needles. Obtained by mixing heptoic aldehyde with an ethereal solution of aniline sulphite (Schiff, *A.* 140, 129).—$C_7H_{13}SO_3NH_3Ph$: usually obtained in attempting to prepare the preceding (Schiff, *A.* 210, 127). Decomposed by water at 65° into $C_6H_{13}.CH:NPh$ and crystalline

$C_6H_{13}.CH(OH).SO_3NH_3Ph$ aq.—

$C_6H_{13}.CH(OH).SO_3.NH_3.CH_2.CO_2H$: crystalline mass, insol. ether, sl. sol. alcohol. Obtained by dissolving heptoic aldehyde in an aqueous solution of glycocoll saturated with SO_2 (Schiff, *A.* 210, 125).

Phenyl-hydrazide $C_7H_{14}:N.NH(C_6H_5)$. (240° at 77 mm.). Oil. Formed by the action of phenyl-hydrazine on œnanthol (Reisenegger, *B.* 16, 663).

Oxim $C_7H_{14}.NOH$. [50°]. (195° cor.). Formed by the action of hydroxylamine (base) on œnanthol (Westenberger, *B.* 16, 2992). Large white tables. Sol. alcohol, ether, and hot water. With Fe_2Cl_6 it gives a rose-red colouration. HCl resolves it into its constituents. By the action of Ac_2O it is converted into the nitrile of heptoic acid (Lach, *B.* 17, 1572).

Ethyl ether $C_7H_{14}.NOEt$. (186°). Oil.

HEPTOLACTONE *v.* *Lactone* of Oxy-heptoic acid.

HEPTONENE C_7H_{10} *i.e.* $CH_2:CH.CH_2.CH:CH.CH:CH_2$. *Heptone.* (115°). From di-allyl-carbinyl chloride and alcoholic KOH (Saytzeff, *A.* 185, 144). Bromine forms liquid $C_7H_{10}Br_6$.

Heptonene $C_5H_{11}.C\vdots CH$. (c. 112°). S.G. $\frac{20}{4}$ ·7458. μ_D 1·4207. From heptoic aldehyde and PCl_5 followed by alcoholic KOH (Brühl, *A.* 235, 10).

Isomeride: Toluene dihydride.

HEPTONITRILE *v.* *Nitrile* of Heptoic acid.

HEPTOYL. The radicle $C_6H_{13}.CO$.

HEPTOYL-ACETIC ALDEHYDE. Sodium derivative $C_6H_{13}.CO.CHNa.CHO$. Obtained by treating methyl hexyl ketone (1 mol.) and formic ether (1 mol.) with NaOEt suspended in ether (Meyerwitz, *B.* 21, 1144). Phenyl-hydrazine converts it into phenyl-hexyl-pyrazole $C_{15}H_{20}N_2$, a thick oil (319°).

HEPTYL. The radicle C_7H_{15}.

Diheptyl *v.* Tetradecane.

HEPTYL ACETATE *v.* Heptyl alcohol.

HEPTYL-ACETIC ACID *v.* Ennoic acid.

Di-heptyl-acetic acid *v.* Hexadecoic acid.

HEYTYL-ACETO-ACETIC ETHER *v.* Aceto-acetic acid.

HEPTYL-ACETONE *v.* Methyl octyl ketone.

***n*-HEPTYL ALCOHOL** $C_7H_{16}O$ *i.e.* $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2OH$. Mol. w. 116. (175·8° i.V.) (Zander, *A.* 224, 84); (176·5° i.V.) (Grimshaw a. Schorlemmer, *C. J.* 26, 1081); (175·5°) (C. F. Cross, *C. J.* 32, 123); (176° cor.) (Perkin). S.G. $\frac{0}{0}$ ·8342 (Z.); $\underline{0}$ ·838 (C.); $\frac{15}{15}$ ·8308; $\frac{25}{25}$ ·8252 (P.). M. M. 7·850 at 12·6°. C.E. (0°–10°) ·00083 (Z.). S.V. 168·3 (Z.). Occurs to a small extent (1·5 g.) in brandy (100 litres) (Ordonneau, *C. R.* 102, 219; *cf.* Faget, *Bl.* 1862, 59).

Formation.—1. By reducing heptoic aldehyde (œnanthol) in acetic acid solution with sodium-amalgam; the resulting heptyl acetate being saponified with potash (Schorlemmer, *A.* 177, 304; *cf.* Bouis a. Carlet, *A.* 124, 352; Jourdan, *A.* 200, 102; Sorabji, *C. J.* 47, 41).—2. By reducing heptoic aldehyde with zinc-dust and HOAc (Krafft, *B.* 16, 1723).—3. From *n*-heptyl chloride (Schorlemmer a. Thorpe, *T.* 174, 270). 4. Among the products of the distillation of sodium ricinoleate with NaOH (Chapman, *Z.* 1865, 737; Wills, *C. J.* 6, 307; Petersen, *A.* 118, 69; Railton, *C. J.* 6, 205).

Properties.—Liquid; gives *n*-heptoic acid on oxidation.

Acetyl derivative $C_7H_{15}OAc$. (191·5° cor.) (Cross); (191·3° cor.) (Gartenmeister). S.G. $\underline{16}$ ·874 (C.); $\frac{0}{0}$ ·8891 (G.). S.V. 221·0. C.E. (0°–10°) ·00096. When obtained by heating heptoic aldehyde (œnanthol) with zinc and glacial HOAc it boils at 180° according to Bouis a. Carlet (*C. R.* 55, 140). The rate of formation of this ether has been studied by Menschutkin (*Z. P. C.* 1, 611).

Methyl derivative $C_7H_{15}OMe$. *Methyl heptyl oxide.* (161°) (W.); (150°) (D.). S.G. $^{16.5}$ ·830 (W.); $\frac{0}{0}$ ·7953 (D.). C.E. (0°–10°) ·001 (Dobriner, *A.* 243, 3). From $NaOC_7H_{15}$ and MeI (Wills, *C. J.* 6, 307).

Ethyl derivative $C_7H_{15}OEt$. *Ethyl heptyl oxide.* (166°). S.G. $\underline{16}$ ·790. From *n*-heptyl iodide and NaOEt (Cross). Wills obtained from $NaOC_7H_{15}$ and EtI a compound (177°); S.G. $\underline{16}$ ·791.

***n*-Iso-heptyl alcohol** $CH_3.(CH_2)_3.CHMe.CH_2OH$ or $(CH_3)_2CH.(CH_2)_3.CH_2OH$. (165°) (G.); (164°) (S.). S.G. $\underline{13.5}$ ·829 (S.). Obtained, together with methyl-iso-amyl-carbinol, by passing dry chlorine into the vapour of boiling isoheptane $(CH_3)_2CH(CH_2)_3CH_3$, converting the resulting mixture of chlorides into acetates, and saponifying these (Grimshaw, *A.* 166, 167; Schorlemmer, *Pr.* 14. 164, 464). It gives a heptoic acid (210°–213°) on oxidation.

Acetyl derivative $C_7H_{15}OAc$. (179°). S.G. $\frac{16\cdot5}{}$ ·871.

Heptyl alcohol $C_7H_{15}OH$. (165°–170°). Obtained by chlorination, &c., from the heptane (90°) which occurs along with *n*-heptane in Pennsylvanian petroleum (Schorlemmer, *C. J.* 26, 319). Perhaps identical with the preceding alcohol. Gives on oxidation a heptoic acid (209°–213°).

Acetyl derivative $C_7H_{15}OAc$. (180°).

Sec-**heptyl alcohol** $CH_3(CH_2)_4CH(OH).CH_3$. *Methyl-amyl-carbinol.* (161°) (Schorlemmer, *C. J.* 26, 319; *A.* 161, 279); (157°) (Schorlemmer a. Thorpe, *T.* 174, 270). Formed from the *sec*-heptyl chloride which is obtained by chlorinating *n*-heptane. Formed also from petroleum heptylene by treatment with cold conc. HClAq, and heating with HIAq at 120° the portion which does not combine with HCl; the resulting iodide is then heated with $Pb(OAc)_2$ and the acetate saponified (Morgan). On oxidation it gives a ketone (151°), and finally acetic and *n*-valeric acid.

Acetyl derivative $C_7H_{15}OAc$. (170°). (Schorlemmer, *A.* 188, 254).

Sec-**heptyl alcohol** $Pr.CH_2.CH_2.CH(OH).CH_3$. *Methyl-isoamyl-carbinol.* (147°); (148°–154°) (P.). S.G. $\frac{17\cdot5}{}$ ·8185. One of the alcohols obtained from isoheptane $Pr.CH_2.Pr$ by chlorination &c. (Grimshaw, *C. J.* 26, 309). Obtained also by reducing methyl isoamyl ketone with sodium amalgam, the yield being 72 p.c. (Rohn, *A.* 190, 309; Purdie, *C. J.* 39, 467). Gives on oxidation methyl isoamyl ketone (143°) and finally acetic and isovaleric acids.

Acetyl derivative $C_7H_{15}OAc$. (167°). S.G. $\frac{23}{17\cdot5}$ ·8595.

Sec-**heptyl alcohol** $C_7H_{15}OH$ *i.e.* $Et.CH(OH).CH_2Pr$. *Ethyl-butyl-carbinol.* (141°). Formed from petroleum heptane by successive conversion into heptyl chloride, heptylene, heptyl chloride, and heptyl acetate (Morgan, *C. J.* 28, 301). On oxidation it gives a ketone (141°), and finally acetic and *n*-butyric acids.

Sec-**heptyl alcohol** $C_7H_{15}OH$. (149°). Formed together with a primary alcohol (165°–170°) from one of the heptanes (90°) in Pennsylvanian petroleum, by chlorination, &c. (Schorlemmer, *C. J.* 26, 319). Gives on oxidation a ketone (142°–146°), and finally nothing but acetic acid.

Sec-**heptyl alcohol** $Pr_2CH.OH$. *Di-propyl-carbinol.* (150°) (K.); (154°) (S.); (155°) (U. a. S.). S.G. $\frac{20}{0}$ ·8188; $\frac{30}{0}$ ·8106 (U. a. K.); $\frac{25}{}$ ·814 (K.); $\frac{0}{}$ ·833. Formed by the action of sodium on di-propyl-ketone mixed with a little water (Friedel, *A. Ch.* [4] 16, 310; Kurz, *A.* 161, 205), or by treating *n*-butyryl chloride with zinc propyl followed by water (Stcherbakoff, *Bl.* [2] 34, 347; 37, 344). Formed also from di-propyl ketone (1 mol.), propyl iodide (3 mols.) and zinc (Ustinoff a. Saytzeff, *J. pr.* [2] 34, 468). Oxidation produces di-propyl-ketone, and finally propionic and butyric acid.

Acetyl derivative (170°–172°). S.G. $\frac{20}{0}$ ·8587. Volatile liquid, with camphor-like odour, sl. sol. water, miscible with alcohol.

Sec-**heptyl alcohol** $Pr_2CH.OH$. *Di-isopropyl-carbinol.* (131°). S.G. $\frac{17}{}$ ·8323. Formed by reducing di-isopropyl-ketone by sodium-amalgam (Münch, *B.* 7, 1370; *A.* 180, 333). Liquid, smelling like peppermint, sl. sol. water, v. sol. alcohol and ether. Chromic acid mixture oxidises it to di-isopropyl-ketone.

Sec-**heptyl alcohol** $Pr.CH_2.CEtH.OH$. *Ethyl-isobutyl-carbinol.* (148°). S.G. $\frac{0}{}$ ·827. Formed by treating isovaleric aldehyde with $ZnEt_2$ and water successively (Wagner, *Bl.* [2] 42, 330). On oxidation it gives ethyl isobutyl ketone, and, finally, acetic and isovaleric acids.

Acetyl derivative $C_7H_{15}OAc$. (163°).

Tert-**heptyl alcohol** CEt_3OH. *Tri-ethyl-carbinol.* (141°–143° i.V.). V.D. 3·74 (for 4·01). S.G. $\frac{20}{0}$ ·8389; $\frac{30}{0}$ ·8299 (B. a. S.); $\frac{0}{}$ ·859 (N.).

Formation.—1. From di-ethyl ketone (1 mol.), EtI (3 mols.) and zinc (Barataeff a. Saytzeff, *J. pr.* [2] 34, 463).—2. From $ZnEt_2$ and propionyl chloride (Nahapetian, *Z.* [2] 7, 274; *A.* 162, 44).

Gives on oxidation CO_2, di-ethyl ketone, heptylene, propionic acid, and acetic acid.

Acetyl derivative $C_7H_{15}OAc$. (160°–163°).

Tert-**heptyl alcohol** $Pr.CH_2.CMe_2OH$. *Di-methyl-isobutyl-carbinol.* (130°). From pseudo-heptylene $Me_2C:CH.Pr$ by passing gaseous HI into the hydrocarbon, and decomposing the resulting iodide with moist Ag_2O (Markownikoff, *Z.* 1871, 268). Formed also by dropping isovaleryl chloride (1 mol.) into cooled zinc methyl (2 mols.), leaving the mixture to itself for a month, and then decomposing it with water (Pawloff, *A.* 173, 192). Colourless liquid, lighter than water and nearly insoluble therein. Smells like camphor. Gives acetic and isobutyric acids on oxidation.

Tert-**heptyl alcohol** $CMe_3.CMe_2OH$. *Di-methyl-tert-butyl alcohol. Penta-methyl-ethyl alcohol.* [17°]. (131°). Formed by the action of $ZnMe_2$ on $CMe_3.CO.Cl$, the product being decomposed by water (Butlerow, *A.* 177, 176). Formed also from α-bromo-isobutyryl bromide by treatment with $ZnMe_2$ followed by water (Kaschirski, *C. C.* 1881, 278); and from $CCl_3.COCl$ (1 mol.) and $ZnMe_2$ (5 mols.) (Bogomoletz, *A.* 209, 78). The oily liquid obtained by any of these processes is distilled with steam, and a hydrate $C_7H_{16}O\frac{1}{2}aq$ is got which crystallises in long prisms, sl. sol. water, v. sol. alcohol and ether; it has a burning taste and an odour like camphor. This hydrate melts at 83° and begins to boil at 100°, giving off water, and at 130° the anhydrous alcohol passes over. The dehydration may also be effected by leaving the hydrate in a closed vessel over baryta at 100°. The anhydrous alcohol is hygroscopic, readily changing to glistening leaflets of the hydrate.

Tert-**heptyl alcohol** $C_7H_{15}OH$ *i.e.* $CHMeEt.CMe_2OH$. (139°). S.G. $\frac{0}{}$ ·8487; $\frac{22}{}$ ·8329. Formed by treating α-bromo-*n*-butyric bromide with $ZnMe_2$ followed by water (Kaschirski, *C. C.* 1881, 278). Oil, smelling like camphor. Gives methyl ethyl ketone, acetone, and HOAc on oxidation. Gives rise to a heptylene (92°–95°).

Tert-**heptyl alcohol** MeEtPrC.OH. *Methyl-ethyl-propyl carbinol.* (135°–138°) (P.); (140°) (S.). S.G. $\underline{20}$ ·823; $\underline{35}$ ·811. From butyryl chloride, $ZnMe_2$, and $ZnEt_2$, followed by water (Pawloff, *A.* 188, 122). Formed also by treating ethyl propyl ketone with MeI and zinc (Sokoloff, *J. R.* 1887, 587). Gives rise to a heptylene (75°–80°). Chromic acid oxidises it to acetic and propionic acids, CO_2, and some ethyl propyl ketone, together with a small quantity of a heptylene C_7H_{14} (97·4°), S.G. $\underline{20}$ ·718; $\underline{30}$ ·709.

Acetyl derivative CMeEtPrOAc. (159°).

Tert-**heptyl alcohol** MeEtᵽrC.OH. (124°–127°). From isobutyryl chloride, $ZnMe_2$, and $ZnEt_2$ (P.). Gives rise to a heptylene (75°–80°).

References.—TETRA-BROMO-HEPTYL ALCOHOL and CHLORO-HEPTYL ALCOHOL.

n-**HEPTYL-AMINE** $C_7H_{15}.NH_2$. (154°) (H.); (156°) (H. a. D.).

Preparation.—1. A mixture of equal mols. of octoic amide and bromine is run into an excess of a 5 p.c. solution of KOH at 60°; the yield is 30 p.c. (Hofmann, *B.* 15, 772; Hoogewerff a. Van Dorp, *R. T. C.* 6, 386).—2. An alcoholic solution of *n*-heptoic aldehyde-phenyl-hydrazide is reduced by means of sodium-amalgam and acetic acid at 25°–30°; the yield is 23 p.c. of the theoretical (Tafel, *B.* 19, 1928).

Properties.—Liquid; forms a carbonate on exposure to the air.—$B'_2H_2PtCl_6$: blackens between 220°–230°.—Picrate $B'C_6H_3N_3O_7$: needles [121°].

Heptylamine $C_7H_{15}NH_2$. (146°). Formed by heating heptyl chloride (from petroleum heptane) with ammonia at 120° for several days; di- and tri-heptylamines being also produced (Schorlemmer, *C. J.* 16, 221; *cf.* Cahours a. Pelouze, *A. Ch.* [4] 1, 5). Light oil, smelling like ammonia, m. sol. water, but separated from its aqueous solution by KOH.—The hydrochloride crystallises in small scales, v. sol. cold water.—$B'_2H_2PtCl_6$: small yellow scales, sl. sol. cold, v. sol. hot, water; sol. alcohol and ether.

HEPTYL-BENZENE $C_{13}H_{20}$ *i.e.* $C_7H_{15}.C_6H_5$. (110° at 15 mm.). Formed, together with $C_7H_{14}(C_6H_5)_2$, by the action of $AlCl_3$ on a mixture of $C_6H_{13}.CHCl_2$ and benzene (Auger, *Bl.* [2] 47, 50; Krafft, *B.* 19, 2982). When nitrated at 20° it gives $C_7H_{15}.C_6H_4.NO_2$ as a yellowish oil (178° at 10 mm.), whence tin and HCl produce $C_7H_{15}.C_6H_4.NH_2$ (175° at 15 mm.).

n-**HEPTYL BROMIDE** $C_7H_{15}Br$. *Bromo-heptane.* (179°). S.G. $\underline{16}$ 1·133. From *n*-heptyl alcohol and HBr (Cross, *C. J.* 32, 123).

Sec-**heptyl bromide** $C_5H_{11}.CHBr.CH_3$. (167°). S.G. $\underline{18}$ 1·422. Prepared by the action of bromine on boiling *n*-heptane (Venable, *B.* 13, 1649). Colourless liquid.

Tert-**heptyl bromide** $Me_3C.CMe_2Br$. [150°]. From penta-methyl-ethyl alcohol and PBr_3 (Kaschirski, *C. C.* 1881, 278). Formed also from $Me_2C{:}CH.CHMe_2$ and HBr. Solid, sol. alcohol, v. e. sol. ether.

n-**HEPTYL CHLORIDE** $C_7H_{15}Cl$ *i.e.* $CH_3(CH_2)_5CH_2Cl$. *Chloro-heptane.* (159°). S.G. $\underline{16}$ ·881. From *n*-heptyl alcohol and HCl (C. F. Cross, *C. J.* 32, 123). Formed also, together with $CH_3(CH_2)_4CHCl.CH_3$, by chlorinating heptane from *Pinus Sabiniana*.

n-*Sec*-**heptyl chloride** $C_7H_{15}C$ *i.e.* $CH_3(CH_2)_4CHCl.CH_3$. Formed as above (Schorlemmer a. Thorpe, *A.* 217, 150). Not obtained free from the preceding, the mixture of the two boiling between 143° and 158°. When chlorine acts upon *n*-heptane (98°), from petroleum, a mixture of heptyl chlorides (145°–160°) is obtained (Schorlemmer, *C. J.* 26, 319; *cf.* Pelouze a. Cahours, *A. Ch.* [4] 1, 5). When passed over heated lime this mixture of chlorides gives a mixture of heptylenes (96°–99°), with one of which HCl combines in the cold, forming a *sec*-heptyl chloride (138°–142°) (Morgan, *A.* 177, 307).

Heptyl chloride $C_7H_{15}Cl$. By chlorinating the isoheptane (90°) in petroleum, there is obtained a mixture of heptyl chlorides (144°–158°), whence KOAc forms a mixture of heptyl acetates (160°–185°), whence a mixture of a primary and a secondary heptyl alcohol may be got (Schorlemmer).

Heptyl chloride $C_7H_{15}Cl$. By chlorinating isoheptane Ᵽr.CH_2.Pr there is formed a mixture of heptyl chlorides (140°–150°), whence KOAc gives a mixture of acetates (160°–175°), from which a primary and a secondary heptyl alcohol may be obtained (Schorlemmer).

Sec-**heptyl chloride** Ᵽr.$CH_2.CH_2$.CHMeCl. (136°). From the corresponding alcohol and HCl (Rohn, *A.* 190, 312).

Tert-**heptyl chloride** $CMe_3.CMe_2Cl$. [135°] (K.); [123°] (E.). From the corresponding alcohol and PCl_5 (Butlerow, *A.* 177, 176; Kaschirski, *C. C.* 1881, 278; Eltekoff, *J. R.* 14, 384). Small crystals. With aqueous $AgNO_3$ it gives a pp. of AgCl.

Tert-**heptyl chloride** CMeEtPrCl. (135°–138°). S.G. $\underline{0}$ ·899. From the alcohol and HCl (Kaschirski, *J. R.* 13, 90).

n-**HEPTYLENE** C_7H_{14} *i.e.* $CH_3(CH_2)_4CH{:}CH_2$. *n-Amyl-ethylene.* Mol. w. 98. (99°). S.G. $^{19\ 5}$ ·703. Formed from *n*-heptane (of petroleum) by chlorinating, and heating the resulting mixture of heptyl chlorides with KOAc and Ac_2O at 160° (Schorlemmer, *C. J.* 26, 322), or by passing them over heated lime (Morgan, *C. J.* 26, 303). The mixture of heptylenes so obtained is treated with HCl, which combines only with ψ-heptylene leaving *n*-heptylene free. *n*-Heptylene occurs amongst the products formed in the preparation of oil gas (Armstrong, *C. J.* 49, 74). *n*-Heptylene combines with HCl when heated with fuming HClAq at 120°. With hydriodic acid at 120° it forms $C_5H_{11}.CHI.CH_3$. With water it forms, according to Le Bel (*C. R.* 81, 967), a hydrate, which is resolved by heat into water, a resin, and an unsaturated alcohol (140°).

ψ-**Heptylene** $C_4H_9.CH{:}CH.CH_3$. (98·5°). The mixture of chloro-heptanes from the heptane of *Pinus Sabiniana*, containing $CH_3(CH_2)_5CH_2Cl$ and $CH_3(CH_2)_4CHCl.CH_3$ if heated with alcoholic KOH at 100° forms a mixture of heptylenes and ethyl heptyl oxides. The heptylene, purified by distilling over sodium, boils at (98·5°). This heptylene, placed with fuming HCl in the dark for six weeks, is but slightly affected, only 10 p.c. combining. On the other hand, petroleum heptylene combines under the same conditions to the extent of 50 p.c. But after several months the first heptylene (from *Pinus*) is almost completely combined with HCl, while more of the petroleum heptylene has combined. Thus cold HCl will not separate isomeric olefines. *Pinus* heptylene is oxidised by H_2SO_4 and $K_2Cr_2O_7$ to valeric and acetic acids only (Schorlemmer a. Thorpe, *A.* 217, 151; *cf.* Venable, *A. C. J.* 4, 22). It rapidly absorbs ClOH in the cold (Grissom, *Am.* 10, 225).

Heptylene C_7H_{14}. From heptylidene chloride and sodium (Limpricht, *A.* 103, 86).

Iso-**heptylene** Pr.CH_2.CH:CH.CH_3. (91°). S.G. ^{15} ·706. From EtC_5H_{11}, by chlorinating and heating the resulting mixture of heptyl chlorides with KOAc and Ac_2O at 160° (Grimshaw, *C. J.* 26, 313). The product, however, is probably a mixture; for a part only combines in the cold with HCl.

Heptylene C_7H_{14} *i.e.* Pr.CH_2.CH_2.CH:CH_2? (75°–80°). From Pr.CH_2.CH_2.CHI.CH_3 and alcoholic KOH (Rohn, *A.* 190, 314).

Heptylene C_7H_{14}. (91°). From the isoheptane in petroleum (Schorlemmer, *C. J.* 26, 320).

ψ-**Heptylene** Pr.CH:CMe_2 or Pr.CH_2.CMe:CH_2. (84°). S.G. ^{0} ·7144. From di-methyl-isobutyl-carbinyl iodide and alcoholic KOH at 100° (Pawloff, *A.* 173, 194). Unites with HI, reproducing the parent iodide.

Heptylene Pr.CH:CMe_2. (82°). S.G. ^{14} ·6995. From oxy-iso-octoic acid $(C_3H_7)_2C(OH).CO_2H$ by heating with water and a few drops of H_2SO_4 at 180° (Markownikoff, *Z.* 1871, 268). Unites with HI, forming PrCMe_2I, and is perhaps identical with the preceding heptylene.

Heptylene CMe_3.CMe:CH_2. (80°). From CMe_3.CMe_2I and alcoholic KOH (Butlerow, *J. R.* 7, 44; Kaschirski, *C. C.* 1881, 278). Formed also by heating CMe_2:CHMe with MeI and PbO at 225° (Eltekoff, *J. R.* 14, 382; *B.* 16, 395). Combines with HI, forming CMe_3.CMe_2I.

Heptylene CMe_2 CMeEt. (75°–80°) (Pawloff, *A.* 188, 122); (92°–95°) (Kaschirski, *C. C.* 1881, 278). S.G. ^{0} ·7355; ^{21} ·7188 (K.). From MeEtPrC.OH.

Heptylene HCEt:CMeEt (?). (90°–95°). From MeEtPrC.OH (P.). Socoloff (*J. R.* 1887, 587) among the products of the oxidation of CMeEtPrOH found a heptylene (97°), S.G. ^{20} ·718 which on further oxidation yielded acetic and propionic acids but no ketone.

Heptylene C_7H_{14}. (96°). S.G. ·742. Occurs in the product of the distillation of colophony, and separated from toluene by sulphonating the latter (Renard, *Bl.* [2] 39, 540; *cf. C. R.* 91, 419; Emmerling, *B.* 12, 1441).

Heptylenes have also been obtained with the following boiling-points: (*a*) by strongly heating paraffin (94°–97°) (Thorpe a. Young, *A.* 165, 11); (*b*) by heating heptoic aldehyde with lime (95°–100°) (Fittig, *A.* 117, 77); (*c*) by heating fusel oil with $ZnCl_2$ (80°–85°) (Wurtz, *Bl.* 5, 307); (*d*) by distilling a lime soap formed from train oil (94° cor.) (Warren a. Storer, *Z.* 1868, 229).

Reference.—Bromo-heptylene.

HEPTYLENE BROMIDE *v.* Di-bromo-heptane.

HEPTYLENIC ACID *v.* Heptenoic acid.

DI-HEPTYL-HEPTOIC ALDEHYDE *v.* Henicosenoic aldehyde.

HEPTYL HYDRIDE *v.* Heptane.

HEPTYLIC ACID *v.* Heptoic acid.

HEPTYLIDENE. The radicle C_6H_{13}.CH.

HEPTYLIDENE DI-ACETONAMINE *v.* Acetonamine.

HEPTYLIDENE-DI-AMINE *Di-benzoyl derivative* $C_{21}H_{26}N_2O_2$ *i.e.* $C_6H_{13}.CH(NHBz)_2$. [128°]. Formed by heating heptoic aldehyde with benzamide (Medicus, *A.* 157, 44). Insol. water, HClAq, and KOH; sl. sol. boiling ether, v. sol. boiling alcohol. Split up by boiling HClAq into benzamide and heptoic aldehyde (œnanthol).

Di-nitro-di-benzoyl derivative $C_6H_{13}.CH(NH.CO.C_6H_4.NO_2)_2$. [170°]. From heptoic aldehyde and nitro-benzoic aldehyde.

HEPTYLIDENE BROMIDE *v.* Di-bromo-heptane.

HEPTYLIDENE CHLORIDE *v.* Di-chloro-heptane.

HEPTYLIDENE THIOCARBIMIDE $C_6H_{13}.CH(NCS)_{22}$. From $C_6H_{13}.CH(NH.CS.NH_2)_2$ by warming with alcohol and HCl (H. Schiff, *B.* 11, 833). Oil, with disgusting odour. Combines with NH_3 reproducing the parent substance.

HEPTYLIDENE-DI-THIO-DI-UREA $C_9H_{20}N_4O_2$ *i.e.* $C_6H_{13}.CH(NH.CS.NH_2)_2$. Formed by adding a drop of HCl to an alcoholic solution of thio-urea and heptoic aldehyde (œnanthol) (H. Schiff, *B.* 11, 833). Decomposed by HCl forming the preceding body.

HEPTYLIDENE-DI-UREA $C_9H_{20}N_4O_2$ *i.e.* $C_6H_{13}.CH(NH.CO.NH_2)_2$. [166°]. Formed by adding heptoic aldehyde (œnanthol) to an alcoholic solution of urea. Small needles; v. sl. sol. alcohol and ether. Decomposed by heat. Boiling dilute acids split it up into urea and heptoic aldehyde. When warmed with an alcoholic solution of benzoic aldehyde there is formed $C_6H_5.CH(NH.CO.NH.CH(C_6H_{13}).NH.CO.NH_2)_2$; a powder insol. water, sl. sol. alcohol and ether (Schiff, *A.* 151, 195).

Di-heptylidene-tri-urea $C_{17}H_{36}N_6O_3$ *i.e.* $(NH_2.CO.NH.CH(C_6H_{13}).NH)_2.CO$. [162°]. Formed by triturating urea with heptoic aldehyde. Crystalline powder. Boiling dilute acids convert into it urea and heptoic aldehyde. Benzoic aldehyde forms $C_6H_5.CH\{NH.CO.NH.CH(C_6H_{13}).NH.CO.NH.CH(C_6H_{13}).NH.CO.NH_2\}_2$, a gelatinous substance that swells up in water (Schiff).

Tri-heptylidene-tetra-urea $C_{25}H_{52}N_8O_4$. [155°]. Formed, together with penta-heptylidene-hexa-urea $C_{41}H_{84}N_{12}O_6$ [c. 150°], by heating either of the preceding ureides with heptoic aldehyde at 100°. Amorphous yellow powder; insol. water, sl. sol. alcohol and ether. Swells up in cold water (Schiff; *cf.* Leeds, *B.* 16, 293, who questions the above formulæ).

n-**HEPTYL IODIDE** $C_7H_{15}I$ *i.e.* $CH_3(CH_2)_5CH_2I$. (203·8°). S.G. $\frac{0}{0}$ 1·4008. S.V. 198·6. C.E. (0°–10°) ·00091. From *n*-heptyl alcohol and HI (Cross, *A.* 189, 4; Dobriner, *A.* 243, 28).

n-*Sec*-**heptyl iodide** $CH_3.(CH_2)_4CHI.CH_3$. (98° at 50 mm.). From the corresponding bromide by treatment with KI (Venable, *B.* 13, 1649). Converted by NaOEt into heptylene. When distilled under atmospheric pressure it splits up into HI and heptylene.

Heptyl iodide $C_7H_{15}I$. (170°). Obtained from heptylene (from petroleum heptane) and HI at 100° for 12 hours (Schorlemmer, *C. J.* 16, 220).

Heptyl iodide $C_7H_{15}I$. (190°). Obtained by the action of iodine and phosphorus on the heptyl alcohol derived from heptane of petroleum (Schorlemmer, *C. J.* 16, 219; *cf.* Petersen, *A.* 118, 74). Heavy oil; alcoholic $AgNO_3$ separates the whole of its iodine as AgI.

Heptyl iodide $C_7H_{15}I$ *i.e.* Pr_2CHI. (180°) (K.); (185°) (F.). S.G. $\frac{20}{}$ 1·2. From di-propyl-carbinol, I, and P (Kurtz, *A.* 161, 205; Friedel, *A. Ch.* [4] 16, 310).

Heptyl iodide $C_7H_{15}I$ *i.e.* $Pr.CH_2.CMe_2I$. From di-methyl-isobutyl-carbinol and HI (Pawloff, *A.* 173, 192). Also from $Me_2CH.CH:CMe_2$ and HI. Heavy oil.

Heptyl iodide $CMe_3.CMe_2I$. [142°]. From the alcohol and HI (Butlerow, *A.* 177, 184; Kaschirski, *C. C.* 1881, 278). Solid, smelling like camphor.

Heptyl iodide $Pr.CH_2.CH_2.CHI.Me$. (165°–175°). From the alcohol and iodide of phosphorus (Rohn, *A.* 190, 313).

Heptyl iodide MeEtPrCI. (146°). S.G. $\frac{0}{}$ 1·93; $\frac{20}{}$ 1·373. From the alcohol and HI (Kaschirski, *J. R.* 13, 90). Suffers much decomposition when distilled.

DI-HEPTYL KETONE $C_{15}H_{30}O$ *i.e.* $(C_7H_{15})_2CO$. [40°]. (178°). Obtained by distilling barium octoate (caprilate) with excess of lime (Guckelberger, *A.* 69, 201). Waxy solid.

n-Sec-**HEPTYL-MALONIC ACID** $C_{10}H_{18}O_4$ *i.e.* $C_5H_{11}CHMe.CH(CO_2H)_2$. [98° uncor.] White crystals. Sol. alcohol, chloroform, and ether, sl. sol. water.

Salts (Leeds, *A. C. J.* 5, 10).—BaA″: white powder, insol. water and alcohol.—CuA″: light-blue crystals, sl. sol. water, sol. alcohol.—PbA″: [235°]. White mass, insol. water, sl. sol. alcohol.—ZnA″: [247°]; minute crystals.—$Ag_2A″$: [244°]; minute crystals, insol. boiling water.

Ethyl ether A′Et. (263°–265°). Colourless liquid. Prepared by the action of *n-sec*-heptyl iodide and sodium on a mixture of alcohol and malonic ether. On heating the acid to 160° it gives heptyl-acetic acid and CO_2 (Venable, *B.* 13, 1651).

HEPTYL OCTYL OXIDE $C_7H_{15}OC_8H_{17}$. (278·8°). S.G. $\frac{0}{0}$ ·8182. S.V. 376·8. C.E. (0°–10°) ·00085 (Dobriner, *A.* 243, 10).

DI-HEPTYL-OXIDE $(C_7H_{15})_2O$. (261·9°). S.G. $\frac{0}{0}$ ·8152. S.V. 352·7. C.E. (0°–10°) ·00098 (Dobriner, *A.* 243, 9).

HEPTYL-UREA *Octoyl derivative* $C_7H_{15}NH.CO.NH.CO.C_7H_{15}$. [102°]. Formed by the action of an alkaline solution of bromine on octoic amide (Hofmann, *B.* 15, 760; 17, 1408).

HERACLEUM OIL. The essential oil of the cow-parsnep (*Heracleum Sphondylium*) is light-green, mobile, S.G. $\frac{20}{}$ ·864, and consists mainly of octyl acetate (200°–212°), whence by saponification octyl alcohol (191°) may be obtained. The portions boiling at a higher temperature contain octyl hexoate (270°) (Zincke, *A.* 152, 1). The oil also contains ethyl butyrate, hexyl acetate, octyl decoate, and octyl laurate in small quantities (Möslinger, *A.* 185, 26). The water with which the oil has been distilled contains methyl alcohol, ethyl alcohol (in smaller quantity), acetic acid, and caproic acid.

The volatile oil of *Heracleum giganteum* is a mixture of octyl acetate, hexyl butyrate, and ethyl butyrate (Franchimont a. Zincke, *B.* 4, 822; *A.* 163, 193; Gutzeit, *A.* 177, 344).

HERACLIN $C_{22}H_{22}O_{10}$. [185°]. S. (alcohol) ·14 in the cold; 1·7 at 78°. S. (CS_2) ·083 in the cold; ·25 at 46°. Occurs in the seeds of *Heracleum giganteum* (Gutzeit, *J.* 1879, 905). Silky needles (from alcohol). Insol. water, v. sol. chloroform, m. sol. ether.

HESPERETIC ACID *v.* ISOFERULIC ACID.

HESPERETIN *v.* HESPERIDIN.

HESPERETOL $C_6H_3(OMe)(OH).CH:CH_2$ [4:3:1]. [57°]. Prepared by the dry distillation of calcium isoferulate (Tiemann a. Will, *B.* 14, 967). Crystalline solid, sol. alcohol and ether. Dissolves in caustic alkalis. Gives a red colouration with H_2SO_4.

HESPERIC ACID $C_{22}H_{28}O_7$. An acid which may be extracted by alcohol from orange-peel (Tanret, *Bl.* [2] 46, 500). Slender white crystals; not volatile; insol. water and ether, sl. sol. cold alcohol, sol. boiling (90 p.c.) alcohol and chloroform. Its K, Na, and Ca salts are amorphous, and decomposed by CO_2.—CaA'_2.

HESPERIDENE $C_{10}H_{16}$. (178° cor.). S.G. $\frac{20}{}$ ·846. A terpene contained in the volatile oil of orange-peel (Wright, *C. J.* 26, 549). It forms a tetrabromide $C_{10}H_{16}Br_4$ [105°], and with NOCl a nitroso- derivative [71°]. Identical with citrene, carvene, limonene, &c. (*v.* TERPENES).

HESPERIDIN $C_{22}H_{26}O_{12}$ (T. a. W.), or $C_{50}H_{60}O_{27}$ (Tanret). [251°]. S. (hot water) ·02 (Hilger, *B.* 9, 26); 1·3 at 100° (T.); S. (alcohol) ·5 in the cold; 1·8 at 78°; S. (EtOAc) ·67 (Tanret, *Bl.* [2] 46, 502). $[\alpha]_D = -89°$. Discovered by Lebreton (*J. Ph.* 14, 377) in many fruits of the genus *Citrus*; thus it may readily be obtained from the white spongy inner coating of the peel of unripe Seville oranges, or from dry unripe bitter oranges (*Citrus Bigaradia*).

Preparation.—Dried unripe orange-peel is thoroughly extracted with water to remove other substances, and the residue then dissolved out with dilute alcoholic NaOH; the impure hesperidin is ppd. from the solution by adding HCl and purified by extraction with alcohol, solution in NaOH, and reppn. with CO_2; the yield is at most 10 p.c. (Tiemann a. Will, *B.* 14, 946).

White minute hygroscopic needles. Nearly insol. alcohol and water, insol. ether. Weak acid, dissolving in aqueous NaOH. It does not react with AcCl, or form a compound with picric acid (Paternò a. Briosi, *G.* 6, 169).

Reactions.—1. On *reduction* with sodium amalgam it gives a body which dissolves in alcohol with a magenta-like colour.—2. By boiling dilute H_2SO_4 it is split up into sugars and hesperitin ($C_{16}H_{14}O_6$). The sugar obtained is a mixture of 2 pts. of glucose with 1 pt. of isodulcite (Tanret, *Bl.* [2] 49, 20); these sugars may be separated by means of their phenyl-hydrazides, that of isodulcite [180°] being soluble in acetone (Will, *B.* 20, 1186).—3. Hesperidin dissolves in dilute KOH, the solution becoming gradually yellow; if it be evaporated to dryness, and the residue be treated with dilute H_2SO_4, it is turned red, and afterwards violet.—4. *Potash-fusion* forms protocatechuic acid.

Hesperetin $C_{16}H_{14}O_6$ *i.e.* [4:3:1] $C_6H_3(OMe)(OH)$ CH:CH.CO.O.$C_6H_3(OH)_2$ [1:3:5]? [226°]. Prepared by heating hesperidin with dilute H_2SO_4 to 120° (E. Hoffmann, *B.* 9, 687; Tiemann a. Will, *B.* 14, 951). White plates.

V. sol. alcohol; m. sol. ether, sl. sol. water, benzene, and chloroform. Weak phenolic acid, dissolving in NaOH, ppd. by CO_2. Has a sweet taste. Like hesperidin, on reduction with sodium-amalgam it gives a substance which dissolves in alcohol forming a magenta-like solution. On boiling with aqueous KOH it decomposes into phloroglucin and isoferulic acid (hesperetic acid). $FeCl_3$ gives a brownish-red colour. Lead acetate gives a pp. Potash-fusion yields protocatechuic acid.

Iso-hesperidin $C_{22}H_{26}O_{12}2aq$ or $C_{50}H_{60}O_{27}5aq$. $[\alpha]_D = -89°$. S. 200 at 100°. S. (90 p.c. alcohol) 11 in the cold. Obtained from orange-peel by extracting with (60 p.c.) alcohol, evaporating, and shaking the residue with chloroform (Tanret, *Bl.* [2] 46, 502; 49, 20). Minute needles from water (containing 2aq), with slightly bitter taste. Sl. sol. cold water, v. e. sol. hot water. Lævorotatory. Split up by boiling dilute H_2SO_4 into hesperitin, dulcite, and glucose. The substance called **hesperidin** by De Vrij is described as NARINGIN.

HETERO-ALBUMOSE *v.* PROTEÏDS.

HEVEENE $C_{15}H_{24}$? (315°). S.G. ^{21} ·921. The least volatile part of the product of the dry distillation of caoutchouc and gutta-percha (Bouchardat, *A.* 27, 30). Amber-yellow oil. Miscible with alcohol and ether. HCl forms unstable $C_{15}H_{24}HCl$. *V.* TERPENES.

n-**HEXADECANE** $C_{16}H_{34}$. *Hecdecane. Di-octyl.* [14°] (E.); [18°] (K.); [20°] (L.); [21°] (Z.). (150° at 10 mm.; 209° at 100 mm.; 288° at 760 mm.); (278°) (Z.; S.); (158° at 15 mm.) (K.). S.G. $^{20}_{4}$ ·774; $^{100}_{4}$ ·719. Odourless solid. Formed by reduction of palmitic acid with P and HI (Krafft, *B.* 15, 1701; 16, 1722; 19, 2218). Also from *n*-octyl iodide and sodium (Lachovitch, *A.* 220, 180; *cf.* Zincke, *A.* 152, 15; Krafft, *B.* 19, 2222); and by heating $Hg(C_8H_{17})_2$ at 200° (Eichler, *B.* 12, 1882). Probably the same hydrocarbon [20°], (278°), V.D. 7·9, is formed by digesting an alcoholic solution of cetyl iodide with zinc and fuming HCl for a week (Sorabji, *C. J.* 47, 37). Pearly plates, sol. hot alcohol and ether.

Hexadecane $C_6H_{13}.CHMe.CHMe.C_6H_{13}$. *Di-iso-octyl.* (263°–265°) (L.); (269° cor.) (A.). S.G. ^{18} ·800 (L.); $^{0}_{4}$ ·802 (A.). V.D. 114·3 (for 113). From secondary octyl bromide (or iodide) and sodium. Liquid smelling of freshly extinguished tallow candles (Lachovitch, *A.* 220, 187; *cf.* Alechin, *Bl.* [2] 40, 186).

Hexadecane $C_{16}H_{34}$. *Cetyl hydride. Cetane.* (280°). V.D. 8·08 (calc. 7·96). Obtained from American petroleum by fractional distillation (Pelouze a. Cahours, *C. R.* 57, 62). Probably identical with *n*-hexadecane.

Reference.—DI-BROMO-HEXADECANE.

HEXADECOIC ACID $HC(C_7H_{15})_2CO_2H$. *Di-n-heptyl-acetic acid.* [26°]. (240°–250°) at 80–90 mm. Obtained by decomposing its ether with concentrated alkalis. Crystalline. Insol. water, sol. alcohol or ether.

Salts.—The salts of the alkalis are soapy and v. sol. water or alcohol. The salts of the alkaline earths and heavy metals have a great tendency to form basic salts.—BaA'_2: slender needles (from alcohol); insol. water.—CuA'_2: bluish-green crystalline pp. [227°].

Ethyl ether EtA'. (c. 310°). From heptyl-aceto-acetic ether, NaOEt, and heptyl iodide (Jourdan, *A.* 200, 114). Oil.

Isomeride *v.* PALMITIC ACID.

HEXADECYL. The radicle $C_{16}H_{33}$, also called CETYL (*q. v.*).

HEXADECYL ALCOHOL *v.* CETYL ALCOHOL.

HEXADECYL ALLOPHANATE $C_{16}H_{33}.O.CO.NH.CO.NH_2$. [70°]. Formed by the action of chloro-formamide on an ethereal solution of cetyl alcohol (Gattermann, *A.* 244, 41). Colourless plates (from alcohol).

HEXADECYL-BENZENE $C_{16}H_{33}.C_6H_5$. [27°]. (230° at 15 mm.). S.G. $^{27}_{4}$ ·8567. From cetyl iodide, iodobenzene, and Na. Sl. sol. cold alcohol, v. sol. ether, benzene, CS_2, and chloroform (Krafft a. Göttig, *B.* 19, 2683; 21, 3180). Gives a nitro- derivative [36°] which reduces to $C_{16}H_{33}.C_6H_4.NH_2$ [53°] (255° at 14 mm.) whence $C_{16}H_{33}.C_6H_4.NHAc$. [104°].

HEXADECYL-CRESOL $C_6H_{13}.C_6H_3Me.OH$. [62°]. (268°). Formed from *p*-hexadecyl-toluene sulphonic acid by potash-fusion at 150°. Crystals (from alcohol).

Ethyl ether $C_6H_{13}.C_6H_3Me.OEt$. [26·5°]. From hexadecyl-cresol, ethyl iodide, and alcoholic KOH (Krafft a. Göttig, *B.* 21, 3180).

HEXADECYLENE *v.* CETENE.

HEXADECYLENE BROMIDE *v.* DI-BROMO-HEXADECANE.

HEXADECYL-MESITYLENE $C_6H_{13}C_6H_2Me_3[6:5:3:1]$. [c. 40°]. (258° at 15 mm.). From bromo-mesitylene, cetyl iodide, and sodium (Krafft a. Gottig, *B.* 21, 3180).

HEXADECYL-PHENOL $C_{16}H_{33}.C_6H_4.OH$. [77·5°]. (261° at 15 mm.). From hexadecyl-benzene by sulphonating and fusing the resulting sulphonic acid with KOH (Krafft, *B.* 19, 2683; 21, 3180).

Ethyl derivative $C_{16}H_{33}.C_6H_4OEt$. [43°]. Plates; gives on oxidation $[4:1]C_6H_4(OEt)(CO_2H)$.

o-**HEXADECYL-TOLUENE** $C_{16}H_{33}.C_6H_4Me[1:2]$. [9°]. (239° at 15 mm.). S.G. $^{22}_{4}$ ·8676; $^{99}_{4}$ ·8072. From *o*-bromo-toluene, cetyl iodide, and sodium (Krafft a. Göttig, *B.* 21, 3181].

m-**Hexadecyl-toluene** $C_{16}H_{33}.C_6H_4Me[1:3]$. [12°]. (237° at 15 mm.). From *m*-bromo-toluene, cetyl iodide, and Na (K. a. G.).

p-**Hexadecyl-toluene** $C_{16}H_{33}C_6H_4Me[1:4]$. [27·5°]. (240° at 15 mm.). Converted by HNO_3 (S.G. 1·2) at 125° into *p*-toluic acid. Fuming H_2SO_4 sulphonates it.

HEXA-DECYL-*m*-XYLENE $C_6H_{13}.C_6H_3Me_2[4:3:1]$. [33·5°]. (250°). From bromo-*m*-xylene, cetyl iodide, and sodium. Crystallises from ether-alcohol (Krafft a. Göttig, *B.* 21, 3180).

HEXA-ICOSANE $C_{26}H_{54}$. [44°]. A soft waxy substance found among the products of the distillation of cerotic acid (Nafzger, *A.* 224, 236).

HEXAÏN DECA-CARBOXYLIC ETHER *v.* HEXANE DECA-CARBOXYLIC ACID.

HEXAMIDINE $C_6H_{14}N_2$ *i.e.* $Pr.CH_2.CH_2.C(NH_2):NH$. *Capronamidine.* Heated with acetic anhydride and sodium acetate it yields the nitrile of hexoic (caproic) acid.

Salts.—B'HCl: large plates [107°], v. sol. alcohol.—$B'_2H_2Cl_2PtCl_4$: yellowish-red plates [199°], sol. hot, sl. sol. cold, water (Pinner, *B.* 17, 175).

HEXAMIDOXIM $C_5H_{11}.C(NOH)NH_2$. *Capramidoxim.* *Isobutylacetamidoxim.* [58°]. Formed by direct combination of hexonitrile (capronitrile) with hydroxylamine. Glistening white silvery tables. V. sol. alcohol, ether, &c., sl. sol. water. Dissolves in aqueous acids and alkalis.—B'HCl: [116°]; white needles, v. sol. water and alcohol, sl. sol. ether.

Ethyl ether $C_5H_{11}C(NH_2)NOEt$: [35°]; very hygroscopic, long white needles; v. sol. alcohol, ether, &c., sl. sol. water.

Acetyl derivative $C_5H_{11}.C(NH_2)NOAc$: [87°]; very fine silky white scales; v. sol. alcohol and ether, nearly insol. water.

Benzoyl derivative $C_5H_{11}C(NH_2)NOBz$: [106°]; felted white needles; sol. alcohol, ether, and benzene, insol. water.

Hexoyl derivative $C_5H_{11}.C(NH_2)NOCOC_5H_{11}$: [115°]; silvery scales; v. sol. alcohol, ether and benzene, sl. sol. water.

Carbonyl derivative $(C_5H_{11}.C(NH_2)NO)_2CO$: [114°]; felted silky needles; v. sol. alcohol and chloroform, nearly insol. water and benzene. Formed by the action of carbonyl chloride upon hexamidoxim (Jacoby, *B.* 19, 1500).

n-**HEXANE** C_6H_{14} *i.e.* $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$. *Di-n-propyl. Hexyl hydride. Methyl-pentane. Methyl-amyl. Ethyl-butane. Ethyl-butyl.* Mol. w. 86. (68·7°) at 751 mm. (Schiff, *A.* 220, 88); (69·0° i.V.) (Zander, *A.* 214, 165); (68·6°) at 744 mm. (Bruhl, *A.* 200, 184); (69°) (Perkin, *C. J.* 45, 446). V.D. 3·06 (calc. 2·99) (Schiff). S.G. $\frac{0}{0}$ ·6753 (Z.); $\frac{17}{4}$ ·6603 (B.); $\frac{10.8}{4}$ ·668 (S.); $\frac{15}{15}$ ·6739; $\frac{25}{25}$ ·6662 (P.). M.M. 6·670 at 11° (P.). S.V. 139·7 (Schiff); 140 (Z.); 138·7 (Ramsay). μ_β 1·3799. R_∞ 47·59 (B.). *Critical temperature* 250·3° (Pawlewsky, *B.* 16, 2634). Occurs in Pennsylvanian petroleum, in the light oils from coal tar (Schorlemmer, *T.* 162, 111), and in Galician petroleum (Lachovitch, *A.* 220, 192). Is the chief constituent of so-called 'petroleum ether' or 'ligroin.'

Formation.—1. By reducing with zinc and dilute HCl the *sec*-hexyl iodide derived from mannite; the product being freed from hexylene by treatment with bromine (Schorlemmer; *cf.* Erlenmeyer, *Z.* 1863, 274).—2. By heating *n*-propyl iodide dissolved in ether with sodium at 145° (Schorlemmer, *A.* 161, 277).—3. By distilling suberic acid with lime or baryta (Dale, *C. J.* 17, 258; *cf.* Riche, *A.* 113, 106).—4. Among the products obtained by distilling tri-oleïn under pressure (Engler, *B.* 22, 596).

Properties.—Oil, with faint characteristic odour, unlike petroleum.

Reactions.—1. On passing through a *red-hot tube* the following products were obtained: ethylene, propylene, butinene C_4H_6, amylene, hexylene, benzene, and gases not absorbed by bromine. Decomposition begins at 600° to 700°, but benzene is not formed except at a high temperature (Norton a. Andrews, *Am.* 8, 1).—2. *Chlorination* gives $CH_3.CH_2.CH_2$ $CH_2.CH_2.CH_2Cl$ and $CH_3.CH_2.CH_2.CH_2.CHCl.CH_3$ (Schorlemmer, *A.* 199, 139; *cf.* Morgan, *C. J.* 28, 301).—3. *Bromine* vapour passed through boiling hexane forms only secondary hexyl bromide (Schorlemmer, *T.* 1878, 1; *A.* 188, 250). Bromine at 125° forms crystalline $C_6H_4Br_6$ and also $C_6H_6Br_6$ and $C_6H_8Br_6$; at 135° it forms C_6Br_8, which, at a higher temperature, is resolved into bromine and hexa-bromo-benzene (Wahl, *B.* 10, 402, 1234).

Sec-**hexane** C_6H_{14} *i.e.* Pr.Pr. *Isohexane. Propyl-isopropyl. Ethyl-isobutyl. Methyl-iso-amyl. Isopropyl-propane.* (62°) (W.); (59°–62°) (Perkin, *C. J.* 45, 447). S.G. $\frac{0}{}$ ·701; $\frac{15}{15}$ ·6633; $\frac{25}{25}$ ·6534 (P.). M.M. 6·769 at 17° (P.). V.D. 3·05 (calc. 2·98). Prepared by decomposing isobutyl iodide (40 g.) with EtI (34 g.) and sodium (11 g.) (Wurtz, *A. Ch.* [3] 44, 275). Occurs in Galician and in American petroleum (Warren; Lachovitch, *A.* 220, 192). By passing through a red-hot tube it is decomposed into ethylene, propylene, butylene, amylene, hexylene, butinene, and some paraffins (Norton a. Andrews, *Am.* 8, 1).

Sec-**hexane** C_6H_{14} *i.e.* Pr.Pr. *Di-isopropyl. Isohexane.* (58·0°) (Zander, *A.* 214, 167). S.G. $\frac{0}{0}$ ·6829 (Z.); ·668 (Perkin, *C. J.* 45, 447). M.M. 6·784 at 15° (P.). S.V. 136·5 (Z.). Formed by the action of sodium on an ethereal solution of isopropyl iodide (Schorlemmer, *A.* 144, 184). Formed also by the action of HI on pinacone $CMe_2(OH).CMe_2(OH)$ (Bouchardat, *C. R.* 74, 809). According to Berthelot (*Bl.* 9, 268) this hexane is also obtained by heating di-allyl with HI. Riche (*A. Ch.* [5] 9, 432) obtained it by distilling barium *n*-heptoate at a red heat. It also occurs among the products obtained by distilling whale oil under pressure (Engler, *B.* 22, 595). It is an oil, with faint odour. Chromic acid oxidises it to CO_2 and acetic acid.

Sec-**hexane** C_6H_{14} *i.e.* $CH_3.CHEt_2$. *Methyl-di-ethyl-methane.* (64°). S.G. $\frac{20.5}{4}$ ·6765. One of the products of the reduction of $CH_3.CHI.CHMeEt$ with zinc and glacial acetic acid $CH_3.C(OH)Et_2$ and $CH_2{:}CH.CHMeEt$ being also formed (Wislicenus, *A.* 219, 315). The same hydrocarbon, (60°), was said by Le Bel (*Bl.* [2] 25, 546) to be formed, together with ethane and decane, by the action of sodium on a mixture of MeI and optically active amyl iodide; Just (*A.* 220, 150) failed, however, to obtain it by this method.

Tert-**hexane** C_6H_{14} *i.e.* CMe_3Et. *Tri-methyl-ethyl-methane.* (43°–48°). From *tert*-butyl iodide and $ZnEt_2$ (Goriainoff, *A.* 165, 107).

References. — DI-BROMO- and DI-CHLORO-HEXANE.

HEXANE CARBOXYLIC ACID *v.* HEPTOIC ACID.

Hexane di-carboxylic acid *v.* DI-ETHYL-SUCCINIC, TETRA-METHYL-SUCCINIC, AMYL-MALONIC, SUBERIC, and DI-ALDANIC ACIDS.

Hexane tri-carboxylic acid $CHEt(CO_2H).CEt(CO_2H)_2$. [150°]. *Ethyl-butenyl tri-carboxylic acid.* Formed by saponifying the ether (1 mol.) with KOHAq (9 mols.) to which a little alcohol has been added (Hjelt, *B.* 21, 2089). Crystalline solid, v. sol. water. At 150°-160° it is split up into CO_2 and di-ethyl-succinic acid.

Ethyl ether Et_3A''' (186° at 36 mm.); (281° at 760 mm.). S.G. $\frac{22.5}{15}$ 1·024.

Formation.—1. By the action of *a*-bromo-butyric ether on sodium ethyl-malonic ether (Hjelt, *B.* 21, 2089; *cf.* Hjelt, *B.* 20, 3078).—2. Sodium (11·5 g.) is dissolved in alcohol

(200 c.c.) and butane tri-carboxylic ether $CH(CO_2Et)_2.CHEt(CO_2Et)$ (137 g.) is added together with EtI (80 g.). The reaction is complete after heating at 100° for 4 hours (Bischoff, *B.* 21, 2092).

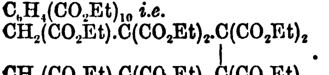
Properties.—Oil, which distils with partial decomposition. By boiling with H_2SO_4 it is saponified, CO_2 being given off, and two isomeric di-ethyl-succinic acids formed, one being v. sol. ether, the other sl. sol. ether.

First nitrile $CO_2Et.CCyEt.CHEt.CO_2Et$. (280°–286°). A product of the action of alcoholic KCy on *a*-bromo-butyric ether (Zelinsky a. Britschinin, *B.* 21, 3398). Oil.

Hexane tri-carboxylic acid $C_6H_{11}(CO_2H)_3$. *Subero-carboxylic acid.* S. 35·6 at 14°. Formed by boiling chloro-suberic acid with KCy and decomposing the resulting cyano-suberic acid with KOH (Gröger, *M.* 1, 510; Bauer, *M.* 4, 341).—$Pb_3A'''_2$ (at 100°).—FeA''': brown pp.—Ag_3A'''.

Hexane tetra-carboxylic acid. *Ethyl ether* $CEt(CO_2Et)_2.CEt(CO_2Et)_2$. *Di-ethyl-acetylene-tetra-carboxylic ether.* (199° at 11 mm.). S.G. $\frac{19}{15}$ 1·043. Formed from chloro-ethyl-malonic ether and sodium ethyl-malonic ether (Bischoff, *B.* 21, 2085). Oil. On saponification it yields di-ethyl-succinic acid [188°].

Hexane deca-carboxylic acid *Ethyl ether* $C_6H_4(CO_2Et)_{10}$ *i.e.*



$$\begin{array}{l}CH_2(CO_2Et).C(CO_2Et)_2.C(CO_2Et)_2\\ \qquad\qquad\qquad\qquad\qquad\quad |\\ CH_2(CO_2Et).C(CO_2Et)_2.C(CO_2Et)_2\end{array}$$

. So-called '*hexaïn*' *decacarboxylic ether.* A thick oil, obtained by treating $CH_2(CO_2Et).C(CO_2Et)_2.C(CO_2Et)_2Cl$ with $CH_2(CO_2Et).C(CO_2Et)_2.C(CO_2Et)_2Na$ (Bischoff, *B.* 21, 2115).

HEXANE SULPHONIC ACID $C_6H_{13}.SO_3H$. Formed by oxidising hexyl mercaptan (from petroleum hexane) (Pelouze a. Cahours, *A.* 127, 192). Syrup.—BaA'_2 (at 100°): scales.

HEXECONTANE $C_{60}H_{122}$. [102°]. Obtained by heating (10 pts. of) myricyl iodide [70·5°] with potassium (1 pt.) at 130°, the product being boiled successively with water, alcohol, petroleum-ether, and glacial acetic acid, and finally crystallised from benzene (Hell a. Hägele, *B.* 22, 502). V. sl. sol. hot alcohol and ether, sl. sol. petroleum-ether and HOAc, m. sol. chloroform and benzene. Partially decomposed by distillation. On distilling under reduced pressure there is formed a paraffin-like mass, v. sol. petroleum-ether, which extracts a hydrocarbon [70°].

HEXENOIC ACID $C_6H_{10}O_2$ *i.e.* $CH_3.CH:CEt.CO_2H$. *a-Ethyl-crotonic acid.* Mol. w. 114. [41°]. (209°).

Formation.—1. From oxalic ether by treatment with $ZnEt_2$ and decomposition of the resulting $CO_2Et.CEt_2.OH$ with PCl_3. By this means the ether is obtained, and is subsequently saponified (Frankland a. Duppa, *C. J.* 18, 133; Fittig a. Howe, *A.* 200, 21).—2. By heating $CO_2Et.CEt_2.OEt$ with HCl at 150° (Geuther, *Bl.* [2] 10, 34).—3. By treating $CO_2H.CEt_2OH$ with PCl_5, and decomposing the distillate with water (Geuther).—4. By distilling oxyhexoic acid $CH_3.CH(OH).CHEt.CO_2H$ (Waldschmidt, *A.* 188, 245).

Properties.—Large four-sided prisms (after fusion); sl. sol. water, v. e. sol. alcohol and ether. Its aqueous solution reddens litmus, but its salts easily give up part of their acid when evaporated. Sublimes in the cold. Readily polymerised by heating or exposing to the air. Not affected by reducing agents.

Reactions.—1. *Potash-fusion* forms acetic and *n*-butyric acid (Petrieff, *B.* 6, 1098).—2. HBr forms $C_6H_{11}BrO_2$ [25°] which when boiled with water or alkalis gives amylene and oxyhexoic acid [48°–52°] (Fittig a. Howe).—3. *Bromine* forms $C_6H_{10}Br_2O_2$ [80·5°].—4. *Chromic acid mixture* forms CO_2 and acetic acid (Chapman a. Smith, *P. M.* [4] 36, 290).—5. $KMnO_4$ added to a very dilute solution of the K salt forms $CH_3.CH(OH).CEt(OH).CO_2H$ [96°] (Fittig, *B.* 21, 919).

Salts. — CuA'_2: greenish-blue pp. — $Cu(OH)A'$: formed from the preceding by heating with alcohol.—PbA'_2 aq: crystalline pp., sl. sol. water.—AgA': scales (from hot water).

Ethyl ether EtA'. (165°). S.G. ^{13} ·920. Mobile oil, smelling of peppermint and of fungi (F. a. D.). Saponified by boiling alcoholic KOH.

Hexenoic acid $C_6H_{10}O_2$ *i.e.* $CH_2Et.CH:CH.CO_2H$ (?). *γ-Ethyl-crotonic acid.* (c. 126° at 26 mm.). From tri-methyl-leucine $Pr.CH_2.CH(NMe_3OH).CO_2H$ by heating at 125° (Körner a. Menozzi, *G.* 13, 354). Liquid. Combines with HBr. Its Cd salts form long prisms.

Hexenoic acid $C_6H_{10}O_2$ *i.e.* $Et.CH:CMe.CO_2H$. *β-Ethyl-methacrylic acid.* [24°]. (213° cor.). S.G. $\frac{25}{25}$ ·9812. One of the products of the oxidation of the corresponding aldehyde (methyl-ethyl-acrolein) (Lieben a. Zeisel, *M.* 4, 70; Solonina, *J. R.* 1887, 302). Monoclinic prisms; $a:b:c = 1·41:1:·385$; $\beta = 104°\ 38'$. Volatile with steam; sl. sol. water, v. e. sol. ether and benzene. Combines with bromine, forming di-bromo-hexoic acid. Reduced by zinc and HBr (or HI) to methyl-propyl-acetic (hexoic) acid. Its soluble salts give white pps. with salts of Zn, Ag, and Pb, a blue pp. with $CuSO_4$, and an oily pp. with $FeCl_3$.—CaA'_2 4aq: prisms or silky needles. — AgA': sparingly soluble needles or leaflets.

Hexenoic acid $C_6H_{10}O_2$ *i.e.* $(CH_3)_2C:CH.CH_2.CO_2H$ or $CH_2:CMe.CH_2.CH_2.CO_2H$. *Pyroterebic acid.* Formed, together with teraconic acid and the lactone of oxy-isohexoic acid, by the dry distillation of terebic acid (Chautard, *J. Ph.* [3] 28, 192; Williams, *B.* 6, 1095; Mielck, *A.* 180, 52). If the process be conducted slowly the lactone is the chief product, if rapidly, pyroterebic acid is mainly produced. The distillate is heated with baryta-water, and CO_2 is passed in until the ppd. $BaCO_3$ is redissolved; the lactone is then extracted with ether, and on evaporating the residue barium teraconate crystallises out. The mother-liquor is treated with H_2SO_4, and pyroterebic acid distilled over with steam, and purified by means of its Ca salt. The yield is about 14 p.c. (Geisler, *A.* 208, 37).

Properties.—Liquid, not solidifying at −15°; sl. sol. water. On adding 3 or 4 vols. of water to the dry acid a homogeneous liquid is obtained, but further addition of water causes separation into two layers, the upper one being the acid. The acid is not affected by boiling for some time with water.

Reactions.—1. Converted by prolonged *heating* at its boiling-point into the isomeric lactone of oxy-isohexoic acid. The same change occurs when HBr is passed into the acid, probably through intermediate formation of the acid $(CH_3)_2CBr.CH_2.CH_2.CO_2H$.—2. *Bromine* forms a di-bromo-isohexoic acid.

Salts.—$CaA'_2$3aq: glistening prisms.—AgA': leaf-like crystals, sl. sol. water.

Hexenoic acid $C_6H_{10}O_2$. Formed by oxidising hexenyl alcohol with chromic acid mixture (Destrem, *A. Ch.* [5] 27, 72). Liquid, volatile with steam. Split up by potash-fusion into acetic and butyric acids. Its salts are amorphous. Probably identical with the preceding acid.

Hexenoic acid $C_6H_{10}O_2$ *i.e.* $CH_2:CMe.CH_2.CH_2.CO_2H$ or $(CH_3)_2C:CH.CH_2.CO_2H$. (203° uncor.). Formed from the lactone of γ-oxy-isohexoic acid by boiling with alcohol and NaOEt for 12 hours (H. Erdmann, *A.* 228, 183). Colourless liquid with pungent odour and acid taste. When boiled for a long time it partially changes to the isomeric lactone of γ-oxy-isohexoic acid.—CaA'_2aq.—$CaA'_2$3aq: trimetric crystals. -AgA'.

Hexenoic acid $C_6H_{10}O_2$ *i.e.* $Pr.CH:CH.CO_2H$(?). *Isopyroterebic acid.* Formed, together with isosorbic acid, by the action of CO_2 on crude C_5H_7Na, possibly through presence of C_5H_9Na as an impurity (Lagermarck a. Eltekoff, *Bl.* [2] 33, 159; *J. R.* 11, 125). Liquid, sl. sol. water; heavier than water. Slightly volatile with steam. Combines with HBr. Bromine forms $C_6H_{10}Br_2O_2$. [99°]. The silver salt dissolves in water.

Hexenoic acid $C_6H_{10}O_2$ *i.e.* $Pr.CH:CH.CO_2H$(?). *Hydrosorbic acid.* (205° cor.); (208° i.V.) (Fittig, *A.* 200, 42). S.G. ^{19} ·969. Formed by reducing sorbic acid with sodium-amalgam (Fittig a. Barringer, *B.* 9, 1198; *A.* 161, 309). Liquid; on prolonged boiling it is decomposed, the boiling-point being raised. Combines with bromine. Combines with fuming HBrAq readily in the cold, forming liquid bromo-hexoic acid (Stahl, *B.* 9, 120). Potash-fusion gives acetic and *n*-butyric acid. On warming with H_2SO_4 it changes to the lactone of oxy-hexoic acid. Its rate of etherification has been studied by Menschutkin (*B.* 13, 163).—CaA'_2aq [c. 125°]. S. (of CaA'_2) 6·2 at 16°. Needles, more sol. cold than hot water.—BaA'_2. [above 265°]. Needles.—CuA'_2: green pp. [185°-190°].—AgA': pp. Sl. sol. cold water.

Ethyl ether EtA'. [167°].

Hexenoic acid $C_6H_{10}O_2$. *Isohydrosorbic acid.* [−10°]. (209° i.V.). Formed, together with the lactone of oxy-hexoic acid, by boiling bromo-hexoic acid (the hydrobromide of hydrosorbic acid) with water (Hjelt, *B.* 15, 618; *cf.* Landsberg, *A.* 200, 51). Combines with HBr, forming the parent bromo-hexoic acid.—CaA'_2aq: laminæ; more sol. hot than cold water.

Hexenoic acid $C_6H_{10}O_2$. *Hexylenic acid.* [39°]. From tri-chloro-hexoic acid, zinc, and HClAq (Pinner, *B.* 10, 1054). Long flat needles (from ether), or lozenge-shaped plates (from ligroin); nearly insol. water, v. sol. alcohol. Does not sublime in the cold.

Hexenoic acid $C_6H_{10}O_2$. (208°). Occurs in small quantity in croton oil (Schmidt a. Berendes, *A.* 191, 121).

References.—Bromo- and Chloro-hexenoic acid.

HEXENOIC ALDEHYDE $C_6H_{10}O$ *i.e.* Et.CH:CMe.CHO. *Methyl-ethyl-acroleïn.* (137° cor.). S.G. $\frac{0}{0}$ 86. Formed by heating propionic aldehyde at 100° with an equal volume of a solution of NaOAc (containing 21 p.c. NaOAc); on fractionally distilling the product the chief portion passes over at 135°-140° (Lieben a. Zeisel, *M.* 4, 16). Colourless liquid, with penetrating odour, insol. water. Gradually turns yellow on exposure to air. It forms a crystalline compound with $NaHSO_3$.

Reactions.—1. HCl forms unstable $C_6H_{11}ClO$. 2. *Bromine* forms $C_6H_{10}Br_2O$, a heavy oil which forms crystalline $C_6H_{10}Br_2(OH)SO_3Na$ 3aq.—3. *Iron filings* and HOAc reduce it to a mixture of a hexyl alcohol $PrCHMe.CH_2OH$, the corresponding aldehyde, and an alcohol $C_6H_{12}O$, which is readily converted into tri-oxy-hexane $Et.CH(OH).CMe(OH).CH_2OH$. — 4. Oxidation with *chromic acid mixture*, free *oxygen*, or moist *silver oxide* gives carbonic, formic, acetic, propionic, hexenoic (ethyl-methacrylic), and di-oxy-hexoic acids, together with methyl propyl ketone.—5. *Ammonia* unites with it, forming a solid product (? $C_{18}H_{36}N_4$ or $C_{12}H_{25}N_3$), which is converted at 140° into parvoline $C_9H_{13}N$, a homologue of pyridine (Waage, *M.* 4, 725). By heating the compound of hexenoic aldehyde with NH_3 to 200° there is formed picoline, parvoline (196°), a base $C_{11}H_{17}N$ (233°), and a base $C_{12}H_{19}N$, which is a mobile liquid, with pale-blue fluorescence. The parvoline gives, on oxidation, pyridine (αβ)-di-carboxylic acid (Hoppe, *M.* 9, 634).—6. Heated with aqueous SO_2 for 4 hours at 80° there is formed, after neutralising with $BaCO_3$, a salt $C_6H_{12}O(SO_3)_2Ba$ 2aq, which is split up by heating with baryta-water into barium sulphite and hexenoic aldehyde. If the contents of the tube are boiled with water before neutralising there is obtained amorphous $C_6H_{12}(SO_3)_2Ba$. 7. If the aldehyde be left in contact with aqueous SO_2 for some days and the product be saturated with $BaCO_3$ and oxidised with bromine water, there is formed a salt of sulpho-hexoic acid: $C_6H_{10}SO_5Ba$ crystallising in hexagonal plates (Ludwig, *M.* 9, 658).

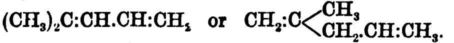
Hexenoic aldehyde $C_6H_{10}O_2$. (135°-138°). Formed, together with allyl chloride and di-allyl-oxide by heating allyl alcohol with dilute (10 p.c.) HClAq at 100° for 20 hours (Solonina, *J. R.* 1887, 302). Oil. Absorbs oxygen eagerly from the air, producing hexenoic (ethyl-methacrylic acid). Forms an oxim [49°] (194°). Probably identical with the preceding aldehyde.

HEXENYL ALCOHOL $C_6H_{12}O$ *i.e.* $CH_2:CH.CH_2.CMe_2OH$. *Di-methyl-allyl-carbinol.* (120° cor.). S.G. $\frac{0}{0}$ ·8438; $\frac{18}{0}$ ·8307. R_∞ 49·84 (Kanonnikoff). H.C. 914,000 (Louguinine, *A. Ch.* [5] 23, 385).

Preparation.—By slowly pouring a mixture of acetone and allyl iodide on granulated zinc at 0° (M. a. A. Saytzeff, *A.* 185, 151, 175). The product is mixed with water and distilled. In the preparation of this body from allyl iodide, zinc, and acetone, a by-product of the formula $C_9H_{18}O$ (c. 176°) occurs if the allyl iodide contains isopropyl iodide. Its specific refractive power, $R_\infty = 72·27$, indicating a double union of carbon atoms. It combines with bromine forming $C_9H_{18}Br_2O$. With PCl_5 it forms $C_9H_{17}Cl$, which boils about 180°, with partial decomposition. The same body is also formed by the action of isopropyl iodide and zinc on the pure hexenyl alcohol (W. Dieff, *J. pr.* [2] 27, 364). A mixture of acetone (75 g.), allyl iodide (205 g.), and isobutyl iodide (230 g.), is converted by zinc into di-methyl-allyl-carbinol, but a small quantity (2 g.) of an alcohol $C_{10}H_{20}O$ (c. 195°) is formed. These bodies appear to be di-methyl-allyl carbinol, in which an atom of hydrogen is displaced by isopropyl and by isobutyl respectively (E. Schatzky, *J. pr.* [2] 30, 216). The alcohol $C_9H_{18}O$ is converted by Na and MeI into a methyl ether $CMe_2(OMe).C_6H_{11}$ (169°–172° uncor.), R_∞ 77·01, S.G. $\frac{21\cdot6}{4}$ ·8027, which is oxidised by $KMnO_4$ to acetic, isobutyric, oxalic, and methoxy-valeric acids (Kononovitch, *J. pr.* [2] 30, 399).

Properties.—Liquid, smelling like camphor; sl. sol. water, with which it forms a hydrate $C_6H_{12}O$ aq (117°).

Reactions.—1. *Chromic acid mixture* oxidises it to formic acid, β-oxy-isovaleric acid, and acetone. $KMnO_4$ acts in like manner (Schirokoff, *J. pr.* [2] 23, 205).—2. *Bromine* forms $C_6H_{12}Br_2O$. 3. HOCl, followed by displacement of Cl by OH, gives tri-oxy-hexane (hexyl-glycerin) (Reformatsky, *J. pr.* [2] 31, 318).—4. By heating the alcohol (1 vol.) with H_2SO_4 (2 vols.) and water (1 vol.) for 3 days at 100°, and distilling the oily product, two hydrocarbons are got, viz. C_6H_{10} boiling below 100°, and $C_{12}H_{20}$ boiling at 180°–200°. The latter is purified by shaking with P_2O_5 and redistilling, and exhibits the following properties: (194°–199°). V.D. 80·3 (H = 1). S.G. $\frac{0}{0}$ ·853; $\frac{21}{0}$ ·839. C.E. (0°–21°) ·00082. R_∞ 89·34. It combines readily with bromine. With fuming HCl it appears to form a compound $C_{12}H_{20},HCl$. It is oxidised by chromic mixture to acetone, acetic acid, propionic acid and a fixed acid with the formula $C_{10}H_{16}O_6$ or $C_{10}H_{14}O_6$ (W. Nikolsky a. A. Saytzeff, *J. pr.* [2] 27, 380). Its specific rotation is 5·22 more than that calculated from Brühl's numbers. This would indicate three C:C groups (Albitzky, *J. pr.* [2] 30, 214). The hydrocarbon C_6H_{10} is formed by removal of H_2O from the alcohol, so that it is either



$$(CH_3)_2C{:}CH.CH{:}CH_2 \quad \text{or} \quad CH_2{:}C\left\langle\begin{matrix}CH_3\\CH_2.CH{:}CH_3.\end{matrix}\right.$$

The hydrocarbon $C_{12}H_{20}$ is a polymeride of this.

Acetyl derivative $C_6H_{11}OAc$. (138° cor.). S.G. $\frac{0}{0}$ ·9007; $\frac{18\cdot5}{0}$ ·8832.

Secondary hexenyl alcohol $CH_2{:}CH.CH_2.CH_2.CH(OH).CH_3$. *Di-allylhydrate. Allyl-isopropyl alcohol.* (139°). S.G. $\frac{18}{17}$ ·842 (Crow); $\underline{0}$ ·861 (Wurtz).

Preparation.—1. Allyl-acetone (1 vol.) is mixed with ether (1 vol.), and put into a flask containing water (2 vols.). Small pieces of sodium are thrown into the flask, which is cooled meanwhile by standing in water. The ethereal solution is poured off, dried over K_2CO_3, and distilled (J. K. Crow, *C. J.* 33, 53; *cf.* Kablukoff, *J. R.* 1887, 513).—2. From hydriodide of di-allyl and Ag_2O (Wurtz, *A. Ch.* [4] 3, 172).

Properties.—Sl. sol. water, v. sol. alcohol and ether. Sweet taste, but rather pungent odour. Combines violently with bromine. Gives acetic acid on oxidation (Sorokin, *J. pr.* [2] 23, 20).

Acetate $C_2H_5.CH_2.CH(OAc)CH_3$. (148°) (Crow); (158° cor.) (Markownikoff, *J. R.* 13, 355). Formed from the alcohol by heating with Ac_2O in a flask with inverted condenser. Formed also from di-allyl di-hydro-iodide and AgOAc. Liquid with pleasant refreshing odour.

Dibromide $CH_2Br.CHBr.CH_2.CH_2.CH(OH)CH_3$. Formed by adding bromine to a solution of the alcohol in $CHCl_3$. The chloroform is then distilled off *in vacuo*. It cannot be distilled. K_2CO_3 converts it into an oil, $C_6H_{11}Br(OH)_2$; volatile with steam.

Hexenyl alcohol $C_6H_{12}O$ *i.e.* $CH_3.CH{:}CH.CMe_2.OH$. (110°–115°). From the chloride of crotonic acid and $ZnMe_2$ (Pawlowsky, *B.* 5, 331).

Hexenyl alcohol $C_6H_{12}O$ *i.e.* $CH_3.CH_2.CH{:}CMe.CH_2OH$. One of the products of the action of iron filings and HOAc on hexenoic aldehyde (methyl ethyl-acrolein). Forms a bromide $C_6H_{12}Br_2O$, which is converted by distillation with water into a tri-oxy-hexane (Lieben a. Zeisel, *M.* 4, 28).

Hexenyl alcohol $C_6H_{12}O$. (137°). S.G. $\underline{10}$ ·891. S. 10 at 10°. Formed by distilling calcium glycerin $CaC_3H_6O_3$ (Destrem, *A. Ch.* [5] 27, 58). Liquid, smelling like peppermint and allyl alcohol. Not reduced by sodium-amalgam. Na and K form gelatinous $C_6H_{11}ONa$ and $C_6H_{11}OK$. Chromic acid oxidises it to pyroterebic acid. Bromine forms $C_6H_{12}Br_2O$ (252°–255°); S.G. $\underline{15}$ 1·99. PCl_5 gives $C_6H_{11}Cl$ (71°). HBr forms $C_6H_{11}Br$ (100°); S.G. $\underline{12}$ 1·35. Chlorine forms $C_6H_{12}Cl_2O$ (205°–210°); S.G. $\underline{12}$ 1·4. PI_3 forms $C_6H_{11}I$ (131°); S.G. $\underline{10}$ 1·92, whence K_2S forms $(C_6H_{11})_2S$ (169°).

Acetyl derivative $C_6H_{11}OAc$. (145°).

Benzoyl derivative $C_6H_{11}OBz$. [105°]. (275°–280°). Yellow prisms.

Reference.—Chloro-hexenyl alcohol.

HEXENYL CHLORIDE $C_6H_{11}Cl$. *Chloro-hexylene.* (71°). From the corresponding alcohol (Destrem, *A. Ch.* [2] 27, 5). Light oil.

Hexenyl chloride $CH_2{:}CH.CH_2.CH_2.CHCl.CH_3$. (130°–140°). Formed, together with di-chloro-hexane, by heating di-allyl (hexinene) with fuming HClAq (Wurtz).

Hexenyl chloride $C_6H_{11}Cl$. (122°). S.G. $\underline{11}$ ·9036. V.D. 4·02. Formed by the action of conc. alcoholic KOH on the di-chloro-hexane, which is a by-product in the action of HOCl on hexylene from mannite (Henry, *C. R.* 97, 260). H_2SO_4 converts it into a ketone $C_6H_{12}O$ (125°); S.G. $\underline{11}$ ·8343; V.D. 3·45.

HEXENYL GLYCERIN *v.* Tri-oxy-hexane.

DI-HEXENYL OXIDE $(C_6H_{11})_2O$. *Diallyl oxide.* (180°). A product of the action of Ag_2O on the mono- or di-hydroiodide of diallyl (Wurtz, *A. Ch.* [4] 3, 175).

Di-hexenyl oxide $(C_6H_{11})_2O$. (117°). From hexenyl iodide and HgO. Also from $C_6H_{11}I$ and $C_6H_{11}ONa$ (*v.* Hexenyl alcohol). Oil, heavier than water (Destrem, *A. Ch.* [5] 27, 58).

DI-HEXENYL SULPHIDE $(C_6H_{11})_2S$. (169°). From iodo-hexylene and K_2S (Destrem, *A. Ch.* [5] 27, 58). Heavy oil, of nauseating odour. Gives a maroon-red colouration with H_2SO_4.

HEXIC ACID $C_7H_{10}O_2$? [126°]. An acid formed from propyl-aceto-acetic ether by successive treatment with bromine and alcoholic KOH (Demarçay, *C. R.* 88, 126; *cf.* Fittig, *B.* 16, 1939; Pawloff, *B.* 16, 486). Large pearly plates (from hot water).

Isohexic acid $C_7H_{10}O_2$? [124°]. Formed in like manner from isopropyl-aceto-acetic ether. Prisms (from ether).

HEXINENE C_6H_{10} *i.e.* Pr.CH_2.C⁝C.H. *Butyl-acetylene.* (70°). Formed by the action of metallic sodium on methyl propyl acetylene at 160°, and decomposition of the sodium compound with water (Faworsky, *J. pr.* [2] 37, 428). Gives pps. with ammoniacal copper and silver solutions. Yields on treating the sodium compound with CO_2 a carboxylic acid.

Hexinene Me_3C.C⁝CH. (39°). Formed by the action of alcoholic potash at 140° for 12 hours on di-chloro-tetra-methyl-ethane (Fawvorsky, *J. pr.* [2] 37, 393). Forms pps. with ammoniacal cuprous and silver solutions. Is not altered by heating with alcoholic potash to 200°.

Hexinene C_6H_{10} *i.e.* CH_2:CH.CH_2.CH_2.CH:CH_2. This compound has been described as DI-ALLYL (*q. v.*). When heated with bromine it gives a crystalline mass [46°]. This is a mixture of two substances, [65°] and [56°], both having the formula $C_6H_{10}Br_4$. From this it appears that the di-allyl obtained by the action of Na on C_3H_5I is a mixture of two isomeric bodies, probably CH_2:CH.CH_2.CH_2.CH:CH_2 and CH_3.CH:CH.CH:CH.CH_3 (dipropenyl) (Sabaneeff, *Bl.* [2] 45, 182). When diallyl is diluted with (1 vol.) paraffin oil and treated with H_2SO_4, the lower layer separated and distilled with water yields 'hexylene oxide,' a liquid $C_6H_{12}O$, smelling like menthol (93°). Oxidation of this $C_6H_{12}O$ gives HOAc and CO_2; sodium-amalgam has no action; HI at 100° gives β-hexyl iodide (166°) (Jekyll, *Bl.* [2] 15, 233). Another method of hydration is to add the diallyl drop by drop to well cooled H_2SO_4. The acid is diluted with ice, neutralised, and distilled, when hexylene oxide passes over at 92°–95°. Some of the salt of the undecomposed sulphuric acid remains behind in the flask. The Ba and Ca salts can be obtained in this way (Béhal, *Bl.* [2] 48, 43).

Hexinene C_6H_{10}. (c. 80°). S.G. ^{12} ·71. V.D. 2·84 (calc. 2·79). Formed from petroleum hexane by bromination, followed by treatment of the resulting hexenyl bromide with alcoholic KOH at 155° (Caventou, *C. R.* 59, 449; Reboul a. Truchot, *C. R.* 65, 73). Forms a liquid dibromide and a crystalline tetrabromide.

Hexinene CH_3.CH_2.CH_2.C⁝C.CH_3? (80°–83°). S.G. $\frac{0}{0}$ ·7494; $\frac{13}{0}$ ·7377. Formed by the action of alcoholic KOH on the hexenyl bromide derived from mannite *viâ* di-bromo-hecane (Hecht, *B.* 11, 1050). Does not ppt. ammoniacal silver or cuprous solutions. Oxidised by chromic acid mixture to acetic *n*-butyric acids.

Hexinene $(CH_3)_2$C:CH.CH:CH_2? (80°). From $(CH_3)_2$CCl.CH_2.CH:CH_2 and alcoholic KOH (M. a. A. Saytzeff, *A.* 185, 157; *v.* HEXENYL ALCOHOL).

Hexinene C_6H_{10}. (c. 80°). In coal tar (Schorlemmer, *A.* 139, 250). Forms $C_6H_{10}Br_4$ [112°].

Hexinene C_6H_{10}. (70°–73°). V.D. 2·97. Obtained, with other products, by passing the vapour of heptinene through an iron tube heated to incipient redness (Renard, *C. R.* 104, 574). Rapidly absorbs oxygen. Does not ppt. ammoniacal $AgNO_3$ or Cu_2Cl_2. Bromine forms unstable, oily $C_6H_{10}Br_2$. Conc. H_2SO_4 polymerises it, forming $C_{12}H_{20}$ (210°–215°).

References.—DI-BROMO- and TETRA-CHLORO-HEXINENE.

HEXINENE GLYCOL *v.* DI-OXY-HEXINENE.

HEXINENE DIOXIDE $C_6H_{10}O_2$ *i.e.*

$$\underset{\diagdown\diagup\atop O}{CH_2.CH}.CH_2.CH_2.\underset{\diagdown\diagup\atop O}{CH.CH_2}$$

. (182°). Formed by acting with KOH on the dichlorhydrin prepared by treating diallyl with hypochlorous acid (Przybytek, *Bl.* [2] 43, 110). Colourless mobile liquid. Heated with water it forms $C_6H_{10}(OH)_4$ sol. alcohol, water, insol. ether. Treated with HCl a dichlorhydrin is formed.

HEXINOIC ACID $C_6H_8O_2$ *i.e.* Pr.C⁝C.CO.OH. [27°]. (125°) at 20 mm. Formed by the action of CO_2 on the sodium compound of propyl acetylene suspended in ether (Fawvorsky, *J. pr.* [2] 37, 419). Feathery crystals. Sl. sol. water, v. sol. alcohol, ether, and petroleum ether. Deliquesces in the air. Decomposes on heating or keeping into CO_2 and propyl-acetylene. Its silver salt at once decomposes in the same way.

Salts.—$(C_6H_7O_2)_2$Ba 3aq. V. sol. water.—A'_2Ca. Thin needles, v. sol. water.—A'_2Cu 2aq. Blue plates, v. sol. water.

Hexinoic acid $C_6H_8O_2$. [93°–96°]. From pyroterebic acid, by successive treatment with bromine and alcoholic KOH (Mielck, *A.* 180, 56). Crystalline mass; m. sol. water. Volatile with steam.—BaA'_2: amorphous.

Hexinoic acid *v.* SORBIC ACID.

Hexinoic acid $C_6H_8O_2$ *i.e.* $(CH_3)_2$.CH.C⁝C.CO_2H. *Iso-sorbic acid.* From Pr.C⁝CNa and CO_2 (Lagermark a. Eltekoff, *J. R.* 11, 125). Liquid. Combines with HBr, forming $C_6H_{10}Br_2O_2$.

Hexinoic acid Pr.C⁝C.CO_2H. *Isopropyl-acetylene carboxylic acid.* [38°]. (107° at 20 mm.). From di-methyl-allylene sodium, and CO_2 (Favorsky, *J. R.* 1887, 553). Should be identical with the preceding.

HEXINYL ALCOHOL $C_6H_{10}O$ *i.e.* C_6H_9OH (140°). A by-product of the action of glycerin on zinc-dust (Claus, *B.* 18, 2931). Forms C_6H_9I (133°).

Acetyl derivative C_6H_9OAc. (127°).

HEXINYL CHLORIDE C_6H_9Cl. *Chloro-diallyl.* (150°). S.G. $\underline{18\cdot2}$ ·9197. V.D. 4·15 (calc. 4·02). A product of the action of PCl_5 upon allyl-acetone (Henry, *C. R.* 87, 171). Oil; combines with bromine, forming oily $C_6H_9ClBr_4$. Alcoholic KOH at 100° forms hexonene (diallylene). This hexinyl chloride is perhaps a mixture of the chloride C_3H_5.CH_2.CCl:CH_2 with C_3H_5.CH:CCl.CH_3.

Hexinyl chloride C_6H_9Cl. (130°). From mesityl oxide, by treatment with PCl_5 and distillation of the resulting $C_6H_{10}Cl_2$ with lime (Baeyer, *A.* 140, 298).

HEXITAMALIC ACID *v.* OXY-HEPTYL-SUCCINIC ACID.

***n*-HEXOIC ACID** $C_6H_{12}O_2$ *i.e.* CH_3.CH_2.CH_2.CH_2.CH_2.CO_2H. *n-Caproic acid.* Mol. w. 116. [−1·5°] (Fittig, *A.* 200, 49). (205°). S.G. $\frac{0}{0}$ ·9446 (Zander, *A.* 224, 67); ·9453 (Gartenmeister, *A.* 233, 277); $\frac{20}{4}$ ·9237 (Brühl). C.E (0°–10°) ·00095 (Z.). S.V. 152·5 (Z.). μ_β 1·4190 R_∞ 50·56 (B.). H.C. 830,209 (Louguinine, *A. Ch.*

[5] 25, 140). *Heat of neutralisation*: Gal a. Werner, *Bl.* [2] 46, 802.

Occurrence.—Among the products of the butyric fermentation of sugar (Grillone, *A.* 165, 167; *cf.* Sticht, *Z.* 1868, 220; Linnemann, *A.* 160, 225; Lieben, *A.* 170, 89).

Formation.—1. By the oxidation of *n*-hexyl alcohol (Zincke a. Franchimont, *A.* 163, 199).—2. By the action of boiling alcoholic KOH on its nitrile (*n*-amyl cyanide) (Lieben a. Rossi, *G.* 1, 314; 3, 27; *A.* 159, 75; 165, 118).—3. Together with other fatty acids by the oxidation of proteïds.—4. From *n*-butyl-aceto-acetic ether and alcoholic KOH (Gartenmeister, *A.* 233, 277).

Preparation.—By fractionally distilling crude fermentation butyric acid, and shaking the portion boiling above 180° with 6 volumes of water.

Properties. — Oil, with faint unpleasant odour.

Reactions.—1. *Oxidised* by nitric acid to acetic and succinic acids (Erlenmeyer, Sigel a. Belli, *B.* 7, 696; *A.* 180, 215).—2. Magnesic caproate in solution subjected to an alternating *electric current* produces butyric, valeric, oxy-caproic, oxalic, succinic, glutaric, and adipic acids (Drechsel, *J. pr.* [2] 34, 135).

Salts.—CaA'_2 aq. S. 2·6 at 18° (Kottal, *A.* 170, 95); 4·6 (Grillone); 2·73 at ·7° (Keppich, *M.* 9, 589).—BaA'_2. S. 9·3 at 18·5° (Lieben a. Rossi); 9·1 at 22° (Grillone); 9·47 at ·5° (Keppich).—$BaA'_2$2aq. S. (of BaA'_2) 12·5 at 10·5° (Lieben a. Janecek, *A.* 187, 128).—$BaA'_2$3aq. S. (of BaA'_2) 12·9 at 23° (K.).—$SrA'_2$3aq: laminæ. S. 9·7 at 24° (K.).—ZnA'_2aq. S. 1 at 24° (K.).—$CdA'_2$2aq. S. 1 at 24° (K.).—CuA'_2. Insol. ether, sol. alcohol.—AgA': pp. (Franchimont a. Zincke, *A.* 163, 200). S. ·077 at 0° (Keppich).

Methyl ether MeA'. (150°). S.G. $\frac{0}{0}$ ·9039. C.E. (0°-10°) ·00105. S.V. 172·2 (Gartenmeister).

Ethyl ether EtA'. Mol. w. 144. (166·6°) (G.). S.G. $\frac{0}{0}$ ·8888. C.E. (0°–10°) ·00103. S.V. 197·7.

Propyl ether PrA'. (186°). S.G. $\frac{0}{0}$ ·8844. C.E. (0°–10°) ·00101. S.V. 222·2.

Butyl ether $Pr.CH_2A'$. (204°). S.G. $\frac{0}{0}$ ·8824. C.E. (0°–10°) ·00099. S.V. 246·0.

n-Hexyl ether $C_6H_{13}A'$. (246° cor.). S.G. $\frac{17·5}{}$ ·865 (Franchimont a. Zincke, *A.* 163, 197).

Heptyl ether $C_7H_{15}A'$. (259°). S.G. $\frac{0}{0}$ ·8769. C.E. (0°–10°) ·00088. S.V. 323·9.

n-Octyl ether $C_8H_{17}A'$. (275°). S.G. $\frac{0}{0}$ ·8748. C.E. (0°–10°) ·00088. S.V. 349·6 (Gartenmeister). Occurs in oil of *Heracleum* (Zincke, *A.* 152, 18).

Chloride $C_6H_{11}OCl$. (c. 138°) (Béchamp, *A.* 130, 364).

Anhydride $(C_6H_{11}O)_2O$. Liquid (Chiozza, *A.* 86, 259).

Acetyl-hexoic anhydride $C_6H_{11}O.OAc$. (165°–175°). Liquid, lighter than water. Formed by heating hexoic acid with Ac_2O (Autenrieth, *B.* 20, 3187).

Amide [100°]. (255°) (Henry, *B.* 2, 490). Plates. Sol. alcohol and hot water. Prepared by heating ammonium hexoate at 230° under pressure; the yield is 70 p.c. (Hofmann, *B.* 15, 983; 17, 1411).

Anilide $C_5H_{11}.CONHPh$. [95°]. Formed by heating the amide with aniline (Kelbe, *B.* 16, 1200). Needles, v. sol. alcohol and ether.

Phenyl hydrazide $C_5H_{11}.CO.NH.NHPh$ [117°].

Nitrile $C_5H_{11}CN$. *n-Amyl cyanide.* Mol. w. 97. (154°). S.V. 141·1 (R. Schiff, *B.* 19, 568). Formed, together with hexylamine, by allowing a mixture of the amide of heptoic acid (1 mol.) and bromine (3 mols.) to run into a 10 p.c. solution of NaOH (Hofmann, *B.* 17, 1410).

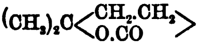
Isohexoic acid $C_6H_{12}O_2$ *i.e.* $Pr.CH_2.CH_2.CO_2H$. *Isocaproic acid. Isobutyl-acetic acid.* (200° i.V.). S.G. ^{22} ·925. *Heat of neutralisation*: Gal a. Werner, *Bl.* [2] 46, 802).

Occurrence.—As glyceryl ether in butter (Chevreul, *Recherches sur les corps gras*), in cheese, and in cocoa-nut oil (Fehling, *A.* 53, 406). Occurs in the free state, together with butyric and valeric acids in the flowers of *Satyrium hircinum*, which have an odour of bugs (Chautard, *Bl.* [2] 2, 56); and, together with several of its lower homologues, in the sarcocarp of *Gingko biloba* (Béchamp, *A.* 130, 364). Found by C. Kraut (*A.* 103, 29) in the water of a brook running out of a peaty soil. Formed also by the fermentation of wheat bran (Freund, *J. pr.* [2] 3, 224).

Formation.—1. By saponifying its nitrile (isoamyl cyanide), which is obtained from isoamyl iodide by boiling with alcohol and calcined K_4FeCy_6 (Frankland a. Kolbe, *A.* 65, 303; Wurtz, *A.* 105, 295).—2. By the action of CO_2 on sodium isoamyl (produced by treating $ZnEt_2$ with sodium) (Wanklyn a. Schenk, *C. J.* 21, 31).—3. By the oxidation of proteïds, fats, and oils, hexoic acid is often formed, but in most cases it has not been determined whether it is *n*- or *iso*-hexoic acid (Redtenbacher, *A.* 59, 41; Schneider, *A.* 70, 112; Arzbacher, *A.* 73, 203; Guckelberger, *A.* 64, 70).—4. From γ-oxy-isohexoic acid by heating with HI and red phosphorus (Mielck, *A.* 180, 45).—5. By decomposing isobutyl-aceto-acetic ether with baryta (Rohn, *A.* 190, 316).—6. Either *n*- or iso-hexoic acid occurs to the extent of 3 p.c. among the acids produced by the fermentation of the perspiration of sheep (yolk). 7. From leucine and nitrous acid.—8. One of the products of the action of zinc isoamyl on oxalic ether (Frankland a. Duppa, *A.* 142, 17).

Properties.—Liquid, with rancid smell. Not solidified by cooling to −18°. When its potassium salt in aqueous solution is decomposed by an electric current decane is produced (Brazier a. Grossleth, *A.* 75, 249).

Reaction.—Oxidised by $KMnO_4$ to γ-oxy-isohexoic acid $(CH_3)_2C(OH).CH_2.CH_2.CO_2H$ which splits off water, giving the lactone



$$(CH_3)_2C\begin{matrix}\diagup CH_2.CH_2 \diagdown \\ \diagdown O.CO \diagup\end{matrix}.$$

Salts.—$CaA'_2$3aq. S. (of CaA'_2) 12·7 at 18·5° (Lieben a. Rossi, *A.* 165, 124); 5·8 at 21° (Mielck); 9·9 at 19° (Rohn).—BaA'_2aq. S. (of BaA'_2) 21 at 22° (Mielck).—$BaA'_2$2aq. S. 53 at 18·5° (L. a. R.); 25 at 14° (Rohn).

Methyl ether MeA'. (150°). S.G. ^{18} ·898 (Fehling, *A.* 53, 410).

Ethyl ether EtA'. (161° cor.). S.G. $\frac{0}{0}$ ·887; $\frac{20}{20}$ ·8705 (L. a. R.).

Isoamyl ether $C_5H_{11}A'$. (215°–220°) (Frankland a. Duppa, *A.* 142, 18).

Amide $Pr.CH_2.CH_2.CONH_2$. [120°]. Prepared by heating ammonium isocaproate at 230°

under pressure; the yield is 63 p.c. of the theoretical (Hofmann, *B.* 15, 983; 17, 1411).

Nitrile $Ꝑr.CH_2.CH_2.CN$. *Isoamyl cyanide.* (155°) (Wurtz, *A.* 105, 296). S.G. ^{29} ·806. V.D. 3·34. Formed by heating isoamyl oxalate, chloride, or iodide with KCy (calcined K_4FeCy_6) (Balard, *A. Ch.* [3] 12, 294; Frankland a. Kolbe, *A.* 65, 288; Brazier a. Gossleth, *A.* 75, 251; Medlock, *A.* 69, 229; Wurtz, *A.* 105, 296). So prepared it is dextrorotatory; $[\alpha]_D = 1·59$, and is therefore impure. It forms the following compounds: $(C_6H_{11}N)_2TiCl_4$. — $(C_6H_{11}N)_2SnCl_2$. — $C_6H_{11}NSbCl_3$.

Hexoic acid $C_6H_{12}O_2$ *i.e.* $CHPrMe.CO_2H$. *Methyl-propyl-acetic acid.* (194° cor.). S.G. ^{25} ·9231; ^{18} ·9279 (Liebermann a. Scheibler, *B.* 16, 1823); $\frac{15}{0}$ ·9286 (Liebermann a. Kleemann, *B.* 17, 918). C.E. ·00075.

Formation.—1. From amylene by combination with HI, treatment of the product with KCy at 115°, and saponification of the product (A. Saytzeff, *B.* 11, 511; *A.* 193, 349).—2. By oxidising $PrCHMe.CH_2OH$ with chromic acid mixture (Lieben a. Zeisel, *M.* 4, 37).—3. By reducing $EtCH{:}CMe.CO_2H$ with HI (L. a. Z.).—4. By reduction of the lactone of γ-oxy-α-methyl-valeric acid (caprolactone) by heating with HI and red phosphorus at 200° (L. a. S.).—5. By the action of *n*-propyl iodide on sodium methyl-aceto-acetic ether and saponification of the product (L. a. K.; E. J. Jones, *A.* 226, 294).—6. From isosaccharin by reduction with HI and P (Kiliani, *B.* 18, 632).—7. In oil of resin, obtained by the dry distillation of colophony (Kelbe a. Warth, *B.* 15, 308).

Properties.—Inactive liquid, sl. sol. water. Weak acid. $FeCl_3$ gives, in a solution of the ammonium salt, a flesh-coloured pp. soluble in excess of the reagent (S.).

Salts.—CaA'_2. Prisms (from alcohol) (S.; L. a. Z. obtained CaA'_2aq).—CaA'_2aq: small needles (from a solution saturated at 50°) (K. a. W.).—$CaA'_2 2\frac{1}{2}aq$: long needles. S. 11·8 at 17°; 7·6 at 100°.—$CaA'_2 3aq$ (L. a. Z.).—$CaA'_2 4aq$ (L. a. Z.).—$CaA'_2 5aq$ (L. a. Z.).—$CaA'_2 8aq$: silky needles (Kiliani). S. (of CaA'_2) 32 at 18·5° (A. Saytzeff, *J. pr.* [2] 23, 293).—BaA'_2: gummy; v. sol. water (S.).—ZnA'_2: more sol. cold, than hot, water (S.). [72°] (K. a. W.).—CuA'_2: green pp.—$CuA'_2Cu_2O_2$: light green pp.—AgA′: slender needles. S ·47 at 20°; ·9 at 100° (S.).

Ethyl ether EtA′. (153° i.V.). S.G. $\frac{0}{0}$ ·8816; $\frac{18}{0}$ ·8670 (A. Saytzeff, *A.* 193, 352).

Hexyl ether $C_6H_{13}A'$. (224° cor.). Formed in the oxidation of $CMePrH.CH_2OH$ by chromic acid mixture (L. a. Z.).

Amide $C_5H_{11}CONH_2$. [95°]. Needles (K. a. W.).—$(C_5H_{11}.CO.NH)_2Hg$. [c. 158°]. Needles.

Hexoic acid $C_6H_{12}O_2$ *i.e.* $CHꝐrMe.CO_2H$. *Methyl-isopropyl acetic acid.* (190°). S.G. ^{15} ·928.

Formation. — 1. From CHꝐrMeI *viâ* CHꝐrMeCN (Markownikoff, *Z.* 1866, 502).—2. From methyl-isopropyl-aceto-acetic ether, obtained by treating aceto-acetic ether successively with NaOEt and ꝐrI followed by MeI; or with MeI followed by ꝐrI. Neither method gives a good yield (Van Romburgh, *R. T. C.* 5, 228).—4. From malonic ether by like processes (R.).

Properties.—Liquid, smelling like its isomerides.

Salts.—CaA'_2. Less sol. hot, than cold, water. S. 20 at 15°. Slender needles (from alcohol).—AgA′: needles (from water).

Amide $C_5H_{11}.CONH_2$. [129°]. Sol. water alcohol, ether, and benzene. Easily sublimed (R.).

Hexoic acid $C_6H_{12}O_2$ *i.e.* $CEtMe_2.CO_2H$. *Dimethyl-ethyl-acetic acid.* [−14°]. (186°). Obtained from the corresponding iodide $CEtMe_2CH_2I$ by heating with potassio-mercuric cyanide, fractionally distilling the resulting nitrile, and then heating it with fuming HCl for 6 days at 100°, and then for 2 days at 120° (Wischnegradsky, *B.* 7, 730; *A.* 174, 56; 178, 103). Formed also by reducing methyl ethyl ketone with sodium amalgam and oxidising the resulting pinacolin $C_8H_{16}O$ with CrO_3 (Lavrinovitch, *A.* 185, 126).

Salts.—$BaA'_2 5aq$: large transparent plates (from water); v. sol. water.—ZnA'_2: white pp.—AgA′: slender needles (from hot water).

Chloride $CMe_2Et.COCl$. (132°).

Nitrile $CMe_2Et.CN$. (130°).

Hexoic acid $C_6H_{12}O_2$ *i.e.* $CEt_2H.CO_2H$. *Diethyl-acetic acid.* (190° i.V.) (Saytzeff). (191°) (Burton, *Am.* 3, 393); (196°) (Schnapp, *A.* 201, 70). S.G. $\frac{0}{0}$ ·936; $\frac{18}{0}$ ·920 (Saytzeff); $\frac{19}{18}$ ·945 (Schnapp).

Formation.—1. From oxy-hexoic ether (di-ethyl-oxalic ether) $CEt_2(OH).CO_2Et$ by treatment with PCl_5 which gives $CEt_2Cl.CO_2Et$, which is then reduced by sodium amalgam (Markownikoff, *B.* 6, 1175). The same chloro-hexoic ether is resolved by distillation into HCl and hexenoic ether, which may be reduced in like manner by sodium-amalgam.—2. From di-ethyl-aceto-acetic ether (Frankland a. Duppa, *A.* 138, 218).—3. By passing CO over a mixture of NaOEt and NaOAc heated to 205° (Fröhlich, *A.* 202, 308).—4. Together with aldehyde, by distilling β-oxy-di-α-ethyl-butyric acid $CH_3.CH(OH).CEt_2.CO_2H$ (Schnapp, *A.* 201, 70), or by treating the same acid with PCl_5 followed by water (Burton). Also from the same acid and HI (B.).—5. From $CHEt_2I$ *viâ* the cyanide (A. Saytzeff, *A.* 193, 349).—6. From di-ethyl-malonic ether (Conrad, *A.* 204, 141).—7. From ethyl-crotonic acid $CH_2{:}CH.CEtH.CO_2H$ by combining with HBr and reducing the resulting bromo-hexoic acid (Howe a. Fittig, *A.* 200, 24; A. Saytzeff, *J. pr.* [2] 23, 288).

Properties.—Liquid; not solidified at −15°.

Salts.—CaA'_2. S. 25 at 23°. Gummy (from water) or twin-crystals (from alcohol).—CaA'_2aq: laminæ. S. (of CaA'_2) 33 at 18·5° (H. a. F.); 30 at ·7° (Keppich, *M.* 9, 589). On evaporating the solution a thin crust forms which dissolves again on cooling. Crystals may be obtained by stirring during evaporation.—$BaA'_2 2aq$.—ZnA'_2: less sol. hot than cold water.—AgA′. S. ·4 at ·7° (Keppich); ·5 at 20°; ·75 at 100°.

Ethyl ether EtA′. (151°). S.G. $\frac{0}{0}$ ·883; $\frac{18}{0}$ ·869 (Saytzeff).

Hexoic acid $C_6H_{12}O_2$ *i.e.* $CHEtMe.CH_2.CO_2H$. *β-Methyl-β-ethyl-propionic acid.* (c. 197°). S.G. ^{15} ·930. $[\alpha]_D = 8·92°$. Formed by oxidising active hexyl alcohol by $K_2Cr_2O_7$ and H_2SO_4 (Van Romburgh, *R. T. C.* 5, 222).

Salts.—$CaA'_2 3aq$: tufts of small needles (from water).—AgA′: needles (from hot solutions).

Hexyl ether $C_6H_{13}A'$. (233°). S.G. ^{15}

·867. $[\alpha]_D = 12·86°$. Formed in the oxidation of the alcohol.

Amide $C_5H_{11}CONH_2$. [124°].

References.—Amido-, Bromo-, and Chloro-hexoic acids.

***n*-HEXOIC ALDEHYDE** $C_6H_{12}O$ *i.e.* $Pr.CH_2.CH_2.CHO$. *n-Caproic aldehyde.* Mol. w. 100. (128° cor.). S.G. $\frac{0}{}$ ·850; $\frac{20}{}$ ·834. Formed by distilling calcium caproate (10 pts.) with calcium formate (7¼ pts.) (Lieben a. Janecek, *A.* 187, 130; *C. J.* 32, 879). Limpid liquid, smelling like aldehyde. Forms a crystalline compound with $NaHSO_3$. Is readily oxidised and readily polymerised.

Hexoic aldehyde $Ᵽr.CH_2.CH_2.CHO$. *Isocaproic aldehyde.* (121°). Formed by distilling sodium formate with sodium isohexoate (Rossi, *A.* 133, 178). Liquid with pungent odour, sl. sol. water, miscible with alcohol and ether. Reduces ammoniacal $AgNO_3$. Gives on oxidation isohexoic (isobutyl-acetic) acid. Reduced by sodium-amalgam to hexyl alcohol (150°). Combines with $NaHSO_3$.

Hexoic aldehyde $C_6H_{12}O$ *i.e.* $Pr.CHMe.CHO$. (116° cor.). From $Et.CH:CMe.CHO$, iron, and dilute HOAc by standing in the cold for a month (Lieben a. Zeisel, *M.* 4, 23). Combines with $NaHSO_3$. Gives $Pr.CHMe.CO_2H$ on oxidation.

Reference.—Tri-chloro- and Di-bromo-hexoic aldehyde.

HEXONENE C_6H_8. (80°–85°). S.G. ·80. Among the products deposited on compressing the gas obtained by heating oils (Couerbe, *J. pr.* 18, 165). The same hydrocarbon (85·5°) occurs in petroleum from Amiano (Dumas, *A.* 6, 257).

Isomeride: Diallylene (*q.v.*). *V.* also Bromo-hexonene.

HEXONITRILE *v. Nitrile* of Hexoic acid.

HEXONYL BROMIDE C_6H_7Br. *Bromo-diallylene.* (150°). From di-bromo-diallyl and KOH (Henry, *B.* 14, 400). Liquid, heavier than water. Combines with bromine. Ppts. ammoniacal $AgNO_3$ and Cu_2Cl_2.

HEXUNENE C_6H_8. [64°]. (130°). V.D. 2·81. Formed by distilling cuprous allylide with an alkaline solution of K_2FeCy_6 (Griner, *C. R.* 105, 283). In presence of CS_2 it combines with bromine forming crystalline $C_6H_8Br_4$ [44°]. It does not ppt. ammoniacal cuprous chloride.

Isomerides. Benzene and Dipropargyl.

DI-HEXYL *v.* Dodecane.

HEXYL ACETATE *v. Acetyl derivative* of Hexyl alcohol.

HEXYL ACETYLENE *v.* Octinene.

***n*-HEXYL ALCOHOL** $C_6H_{14}O$ *i.e.* $Pr.CH_2.CH_2.CH_2OH$. Mol. w. 102. (157° cor.). S.G. $\frac{0}{0}$ ·832. C.E. (0°–10°) ·00087. S.V. 146·2 (Zander, *A.* 224, 82). Occurs in fusel oil from brandy (Faget, *A.* 88, 325) to the amount of ·6 p.c. (Ordonneau, *C. R.* 102, 219). *n*-Hexyl acetate and butyrate occur in the essential oil of *Heracleum* (Franchimont a. Zincke, *B.* 4, 822; *A.* 163, 193; Möslinger, *A.* 185, 41). Perhaps the hexyl alcohol in these cases is $Ᵽr.CH_2.CH_2.CH_2OH$.

Formation.—1. Through the acetate, from *n*-hexyl chloride which is formed, together with *sec*-hexyl chloride, by chlorinating hexane (Cahours a. Pelouze, *C. R.* 54, 1245; Schorlemmer, *A.* 161, 271).—2. By reducing the corresponding aldehyde with sodium-amalgam (Lieben a. Rossi, *A.* 133, 178; Lieben a. Janecek, *A.* 187, 126).

Formyl derivative $C_6H_{13}OCHO$. (146°). S.G. $\frac{17}{}$ ·8495. Smells like apples.

Acetyl derivative $C_6H_{13}OAc$. (170° i.V.). S.G. $\frac{17·5}{}$ ·889 (F. a. Z.); $\frac{0}{0}$ ·8902. C.E. (0°–10°). ·00100. S.V. 197·7 (Gartenmeister).

Benzoyl derivative $C_6H_{13}OBz$. (272°). S.G. $\frac{17}{}$ ·998. Oil, smelling like apples (Frentzel, *B.* 16, 745).

Hexoyl derivative $C_6H_{13}O.CO.C_5H_{11}$. (246°). S.G. $\frac{17·5}{}$ ·865.

Ethyl ether $C_6H_{13}OEt$. (134°–137°).

Isohexyl alcohol $Ᵽr.CH_2.CH_2.CH_2OH$. (150°). Formed by reducing the corresponding aldehyde with sodium amalgam (Rossi, *A.* 133, 180).

Hexyl alcohol $CH_3.CH_2.CHMe.CH_2.CH_2OH$. *β-Ethyl-butyl alcohol.* (154° cor.). S.G. $\frac{15}{}$ ·829. $[\alpha]_D = 8·2°$. Obtained among the products of saponification of Roman oil of chamomile (Van Romburgh, *R. T. C.* 5, 220). Gives on saponification a dextrorotatory hexoic acid and a hexyl hexoate (234°), S.G. $\frac{15}{}$ ·867, $[\alpha]_D = 12·86$ at 19°.

Hexyl alcohol $CH_3.CH_2.CH_2.CHMe.CH_2OH$. *a-Propyl-propyl alcohol.* (147°). S.G. $\frac{0}{0}$ ·8375. One of the products of the reduction of $CHEt:CMe.CHO$, and separated from the accompanying $CHEt:CMe.CH_2OH$ by treatment with bromine and water, whereby the latter is changed to $CHEt(OH).CMe(OH).CH_2OH$ (Lieben a. Zeisel, *M.* 4, 28). Optically inactive liquid. On oxidation with chromic acid mixture it yields $CH_2Et.CHMe.CO_2H$ and methyl propyl ketone.

Acetyl derivative $C_6H_{13}OAc$. (162° cor.). S.G. $\frac{25}{25}$ ·8717.

Hexyl alcohol $Ᵽr.CHMe.CH_2OH$ (?). (153° i.V.). S.G. $\frac{15}{}$ ·830. Occurs as angelate and tiglate in Roman oil of chamomile (Köbig, *A.* 195, 102). Formed also from Ᵽr.Ᵽr by chlorination, &c. (Silva, *B.* 6, 147).

Acetyl derivative $C_6H_{13}OAc$. (155°–160°).

***Sec*-hexyl alcohol** $CH_3.CH_2.CH_2.CH_2.CHMe.OH$. *Methyl-butyl-carbinol.* (*β*)-*Hexyl alcohol.* (137°) (E. a. W.); (141°) (S.). S.G. $\frac{0}{}$ ·833; $\frac{16}{}$ ·821.

Formation.—1. By digesting (*β*)-hexyl iodide with water and Ag_2O (Wanklyn a. Erlenmeyer, *C. J.* 16, 221; Hecht, *A.* 165, 146), or with a large excess of boiling water (Niederist, *A.* 196, 351).—2. From the corresponding chloride which is formed together with *n*-hexyl chloride by chlorinating *n*-hexane (Schorlemmer, *A.* 161, 272).—3. From the mixture of chlorides obtained from *n*-hexane by conversion into hexylene and treatment with HCl (Morgan, *A.* 177, 307).—4. By converting (*β*)-hexyl iodide into hexylene, treating the product with H_2SO_4 and distilling the resulting $C_6H_{13}O.SO_3H$ with water (W. a. E.).—5. Formed also by treating hexylene from mannite with HOCl and reducing the product with iron filings and acetic acid (Domac, *M.* 2, 320; *A.* 213, 124).

Properties. — Thick liquid with pleasant odour, very unlike that of isoamyl alcohol. Chromic acid mixture oxidises it to an aldehyde, and afterwards to butyric and acetic acids.

Acetyl derivative $C_6H_{13}OAc$. (156° cor.). S.G. $\frac{0}{}$ ·878.

Ethyl ether $C_6H_{13}OEt$. (133°). S.G. $\frac{19}{}$ ·776.

***Sec*-hexyl alcohol** $CH_3.CH_2.CHMe.CHMe.OH$. *Methyl-sec-butyl-carbinol.* (134° i.V.). S.G. $\frac{19}{4}$ ·8307. Formed by reducing methyl *sec*-butyl ketone dissolved in wet ether by sodium. A pinacone $C_{12}H_{26}O_2$ (249°) is also formed, and this, when warmed with dilute H_2SO_4 gives two pinacolines $C_{12}H_{21}O$ (Wislicenus, *A.* 219, 319). Colourless oil.

***Sec*-hexyl alcohol** $CH_3.CH_2.CH(OH).CH_2.CH_2.CH_3$. *Ethyl-propyl-carbinol.* (135° cor.). S.G. $\underline{0}$ ·834; $\underline{20}$ ·819. Formed by reducing ethyl propyl ketone by sodium-amalgam (Völker, *B.* 8, 1019; Oechsner de Coninck, *Bl.* [2] 25, 7; *B.* 9, 193). Gives on oxidation ethyl propyl ketone and propionic acid.

Acetyl derivative $C_6H_{13}OAc$. (150°).

Hexyl alcohol $C_6H_{14}O$. (138°). From di-chloro-di-ethyl oxide $CH_2Cl.CHCl.OEt$ by treatment with $ZnEt_2$ and treatment of the resulting $CH_2Et.CHEt.OEt$ with HI, KOAc, and KOH successively (Lieben, *A.* 178, 22). Gives acetic and butyric acids on oxidation, and would therefore appear to be identical with methyl-butyl-carbinol.

Ethyl ether $C_6H_{13}OEt$. (131°). S.G. $\underline{0}$ ·787; $\underline{20}$ ·770.

***Sec*-hexyl alcohol** $(CH_3)_3.C.CHMe.OH$. *Methyl-tert-butyl-carbinol.* [4°]. (120·5°). S.G. $\underline{0}$ ·635. Formed by reducing the corresponding ketone (pinacolin) with sodium-amalgam (Friedel a. Silva, *C. R.* 76, 226). Liquid smelling like camphor, solidifying in a freezing-mixture to a mass of long silky needles. Oxidised by chromic mixture to pinacolin and tri-methyl-acetic acid.

Acetyl derivative $C_6H_{13}OAc$. (c. 142°).

***Tert*-hexyl alcohol** $CMeEt_2OH$. *Methyl-di-ethyl-carbinol.* (123°). S.G. $\frac{20}{0}$ ·8237; $\frac{25}{0}$ ·8194; $\frac{35}{0}$ ·8104.

Formation.—1. By treating acetyl chloride with $ZnEt_2$, leaving the product for two days until it has become viscid; then heating to 100° and mixing with water (Butlerow, *Bl.* [2] 5, 17). 2. Together with hexylene, hexane, and other products by treating $CH_3.CHI.CHMeEt$ dissolved in alcohol with HOAc and zinc (Wislicenus, *A.* 219, 315).—3. From the corresponding iodide $CMeEt_2I$ and cold very dilute KOHAq (W.).—4. By acting on di-ethyl ketone (1 mol.) with MeI (3 mols.) and zinc, followed by water (Reformatsky, *J. pr.* [2] 36, 340). Colourless mobile liquid, smelling like *tert*-butyl alcohol. Chromic acid mixture oxidises it to acetic acid only.

Acetyl derivative $CMeEt_2.COAc$. (148° cor.). S.G. $\frac{20}{0}$ ·8824; $\frac{25}{0}$ ·8772; $\frac{35}{0}$ ·8679.

***Tert*-hexyl alcohol** $CMe_2Pr.OH$. *Di-methyl-propyl carbinol.* (115°) (B.); (123°) (J.). Formed by treating butyryl chloride with $ZnMe_2$ followed by water (Butlerow, *Z.* 1865, 617; Jawein, *A.* 195, 254). Rather viscid liquid, lighter than water, and somewhat soluble therein. Does not solidify at −38°. Gives on oxidation acetic and propionic acids.

***Tert*-hexyl alcohol** CMe_2PrOH. *Di-methyl-isopropyl-carbinol.* (113°) (P.); (117°) (Pavloff, *A.* 196, 123); (119°) (K.). S.G. $\underline{0}$ ·836; $\underline{12}$ ·823 (P.); $\underline{0}$ ·837 (K.). C.E. (0°–50°) ·00099.

Formation.—1. By treating isobutyryl chloride with $ZnMe_2$ followed by water (Prianischnikoff, *Bl.* [2] 16, 303).—2. From α-bromo-propionyl bromide by successive treatment with $ZnMe_2$ and water (Kaschirski, *C.C.* 1881, 278).—3. By acting on $ZnMe_2$ (5 pts.) with chloral (2 pts.) (Rizza, *Bl.* [2] 38, 164).—4. From $ZnMe_2$ and di-chloro-acetyl chloride, the yield being 6 p.c. (Bogomoletz, *Bl.* [2] 34, 3[illegible]0).

Properties.—Liquid, smelling of camphor, solidifying at −14°. On oxidation with chromic acid mixture it gives acetone and acetic acid.

References. — Bromo- and Chloro-hexyl-alcohol.

(*n*)-HEXYL-AMINE $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.NH_2$. (129°). S.G. $\underline{17}$ ·77. Occurs in cod-liver oil (Gautier a. Mourgues, *C. R.* 107, 254). Obtained from *n*-hexyl chloride (derived from *n*-hexane in petroleum) and NH_3 (Pelouze a. Cahours, *A. Ch.* [4] 1, 5).

Preparation.—A mixture of equal mols. of the amide of hexoic acid and bromine is run into an excess of a 10 p.c. solution of KOH at 60°; the yield is 70 p.c. (Hofmann, *B.* 15, 771; Frentzel, *B.* 16, 744).—B'HCl: laminæ.—$B'_2H_2PtCl_6$: scales.

Isohexyl-amine $Pr.CH_2.CH_2.CH_2NH_2$. From isohexyl iodide and alcoholic NH_3 (Rossi, *A.* 133, 181).—$B'_2H_2PtCl_6$: scales.

(β) - Hexylamine $Pr.CH_2.CHMe.CH_2NH_2$. (116° i.V.). S.G. ·76. Formed, together with hexylene, by heating (β)-hexyl iodide with NH_3 (Uppenkamp, *B.* 8, 56; Jahn, *B.* 15, 1292; *M.* 3, 170).—$B'_2H_2PtCl_6$: golden plates.

***Tert*-hexylamine** $CMeEt_2NH_2$. (109°). From the carbamine $CMeEt_2NC$ and HClAq (Schdanoff, *A.* 185, 123).

Di-*n*-hexyl-amine $(C_6H_{13})_2NH$. (190°–195°). From alcoholic NH_3 and *n*-hexyl chloride derived from *n*-hexane of petroleum (P. a. C.).

Tri-*n*-hexyl-amine $(C_6H_{13})_3N$. (260°). From *n*-hexyl chloride and alcoholic NH_3 (P. a. C.). Formed also by distilling with lime the compound of heptoic aldehyde (œnanthol) with NH_3 and SO_2 (Petersen, *A.* 101, 310; 102, 312).—B'HCl.—$B'_2H_2PtCl_6$: glittering laminæ.

Ethylo-iodide $(C_6H_{13})_3NEtI$: liquid.

HEXYL-BENZENE $Ph.CH_2.CH_2.CH_2CH(CH_3)_2$. *Capryl-benzene.* (212°–213°) at 733 mm. S.G. $\underline{16}$ ·857. From benzyl bromide, iso-amyl bromide, benzene, and sodium (Schramm, *A.* 218, 391; *cf.* Aronheim, *A.* 171, 223).

Reaction.—Bromine vapour at 150° forms $PhCHBr.CH_2.CH_2.CH(CH_3)_2$, which, on distillation, gives HBr and phenyl-hexylene, whose dibromide $Ph.CHBr.CHBr.CH_2.CHMe_2$ forms needles or plates [79°–80°].

Reference.—Di-bromo-hexyl-benzene.

***n*-HEXYL BROMIDE** $C_6H_{13}Br$. (156° cor.). S.G. $\underline{0}$ 1·194; $\underline{20}$ 1·173. From *n*-hexyl alcohol and HBr (Lieben a. Janecek, *A.* 187, 137).

Hexyl bromide $Pr.CHMe.CH_2Br$. (c. 144° cor.). From the corresponding alcohol and conc. HBrAq at 130° (Lieben a. Zeisel, *M.* 4, 33). Converted by water (30 pts.) at 150° into hexylene.

***Sec*-hexyl bromide** $Pr.CH_2.CHMeBr$. [144°]. From boiling *n*-hexane and bromine (Schorlemmer, *A.* 188, 250).

HEXYL-CHLORAL *v.* Tri-chloro-hexoic aldehyde.

***n*-HEXYL CHLORIDE** $C_6H_{13}Cl$ *i.e.* Pr $CH_2.CH_2.CH_2Cl$. *Chloro-hexane.* (133°) (Lieben a. Janecek, *A.* 187, 139; Frentzel, *B.* 16, 745). Formed, together with (β)-hexyl chloride, by chlorinating *n*-hexane (Cahours, *C. R.* 10, 1241).

Sec-**hexyl chloride** $CH_3.CHCl.CH_2.CH_2.CH_2.CH_3$. (β)-*Hexyl chloride.* (125°). From cold fuming HCl and hexylene, derived from *n*-hexane (got from mannite) by chlorination and subsequent treatment with alcoholic potash (C. Schorlemmer, *Pr.* 29, 365; *T.* 171, 452; Domac, *M.* 2, 313). Formed also, together with *n*-hexyl chloride, by chlorinating *n*-hexane (Schorlemmer, *A.* 161, 272), and by saturating (β)-hexyl alcohol with HCl and heating in a sealed tube at 100° (Erlenmeyer a. Wanklyn, *C. J.* 17, 190). With $Pb(OAc)_2$ and glacial acetic acid at 125° it forms hexyl acetate $C_6H_{13}OAc$. If this is ppd. by water and saponified by strong potash an alcohol or mixture of alcokols (130°–140°) is got. This alcohol gives on oxidation acetic and butyric, but no propionic acid.

Hexyl chloride Ᵽr.CHMe.CH_2Cl. (124°). A product of the chlorination of Ᵽr.Ᵽr (Silva, *Bl.* [2] 6, 36; 7, 953).

Sec-**hexyl chloride** $C_6H_{13}Cl$. (117°). Formed by passing HCl through a mixture of conc. HClAq and the mixed hexylenes obtained by the action of alcoholic KOH upon the mixture of hexyl chlorides got by chlorinated *n*-hexane (Morgan, *C. J.* 28, 301). The same hexyl chloride is probably also got from the hexylene found among the products of the distillation of glycerin with NaOH (Fernbach, *Bl.* [2] 34, 146). The corresponding alcohol boils at 125°–129°, and gives on oxidation a ketone (c. 123°).

Sec-**hexyl chloride** $C_6H_{13}Cl$. (123°). Obtained by heating with HClAq for 10 hours at 135° the hexylene left uncombined in preparing the preceding hexyl chloride (M.). Probably identical with (β)-hexyl chloride. When heated with $Pb(OAc)_2$ and HOAc at 120° it gives a hexyl acetate which, on saponification, yields a hexyl alcohol (132°–137°), which is oxidised by chromic acid mixture, even in the cold, to a ketone (125°).

Sec-**hexyl chloride** CMe_3.CHMe.Cl. (114°). S.G. $^{\underline{0}}$ ·899; $^{\underline{25}}$ ·875. From the corresponding alcohol and HCl (Friedel a. Silva, *Bl.* [2] 19, 289).

Tert-**hexyl chloride** CMe_2PrCl. (100°). From the alcohol and PCl_5 (Butlerow, *J.* 1864, 497). Partially decomposed on distillation.

Tert-**hexyl chloride** CMe_2ᏢrCl. [–2°]. (111°). S.G. $^{\underline{0}}$ ·897; $^{\underline{12}}$ ·878. From CMe_2:CMe_2 and HCl (Pawloff, *A.* 196, 124; Kaschirski, *C. C.* 1881, 278). Also from ᏢrᏢr and Cl (Silva).

Tert-**hexyl chloride** $CMeEt_2Cl$. (110°). From the alcohol and PCl_5 (Butlerow).

Hexyl chloride $C_6H_{13}Cl$. (122°). S.G. $^{\underline{14}}$ ·8943. From di-isopropyl (hexane) ᏢrᏢr and chlorine (Schorlemmer, *A.* 144, 184). Silva (*Bl.* [2] 6, 36; 7, 953) obtained, however, CMe_2ᏢrCl (118°) and Ᏻr.CHMe.CH_2Cl (124°).

HEXYL-CYANIC ACID *v.* CYANIC ACID.

***n*-HEXYLENE** C_6H_{12} *i.e.* $CH_3.CH_2.CH_2.CH_2.CH:CH_2$. *Butyl-ethylene.* (α)-*Hexylene.* Mol. w. 84. (69°). From *n*-hexyl chloride and alcoholic KOH (Morgan, *A.* 177, 305; Schorlemmer, *A.* 199, 141). The same hexylene is perhaps formed by treating the di-hydro-di-iodide with sodium. It boils at 69°, and has S.G. $^{\underline{0}}$ ·694 (Wurtz, *A. Ch.* [4] 3, 129). Greville Williams (*T.* 1847; *A.* 108, 384) found a hexylene boiling at 71° among the products of the distillation of Boghead coal. Thorpe and Young (*A.* 165, 8) obtained a hexylene boiling about 65° to 70° from strongly heated paraffin. *n*-Hexylene is among the products of the manufacture of oil gas (Armstrong, *C. J.* 49, 74).

Properties.—*n*-Hexylene does not combine with fuming HCl in the cold; but at 100° it forms hexyl chloride (123°). With bromide of nitrogen it forms a heavy oil (A. K. Miller, *C. J. Proc.* 3, 110).

(β)-Hexylene $CH_3.CH_2.CH_2.CH:CH.CH_3$. (69°) (W. a. E.); (67°) at 738 mm. (Hecht a. Strauss, *A.* 172, 62). S.G. $^{\underline{0}}$ ·700. V.D. 2·92 (calc. 2·90). Obtained, apparently in the pure state, from the *n*-hexane derived from mannite by chlorinating and heating the resulting mixture of hexyl chlorides (121°–134°) with alcoholic KOH at 100° (Schorlemmer, *Pr.* 29, 365). Formed also by treating (β)-hexyl iodide with alcoholic KOH at 100° (Erlenmeyer a. Wanklyn, *A.* 135, 141; *cf.* Hecht, *B.* 11, 1050), and, together with the preceding, from the *n*-hexane of petroleum by chlorination, followed by treatment with alcoholic KOH (Morgan, *A.* 177, 305; *C. J.* 28, 301). Also from (β)-hexyl iodide and $ZnMe_2$ at 125° (Purdie, *C. J.* 39, 465).

Reactions.—1. Combines with cold fuming HClAq; the combination being complete in the course of a few weeks, the product being $CH_3.CH_2.CH_2.CH_2.CHCl.CH_3$ (125°) (Schorlemmer).—2. HI forms (β)-hexyl iodide (168°).—3. Chromic acid mixture oxidises it to *n*-butyric and acetic acids.—4. ClO_2 gas (from $KClO_3$ (2 pts.), $H_2C_2O_4$ 2aq (1 pt.), H_2SO_4 (1 pt.), and H_2O (2 pts.)) forms acetic and butyric acid, and a body that can be reduced by nascent hydrogen to secondary hexyl alcohol (Domac, *A.* 213, 124). 5. HClO gives $C_6H_{12}Cl(OH)$ (140°) (Domac, *M.* 2, 309).—6. H_2SO_4 (3 pts.), diluted with water (1 pt.), dissolves (β)-hexylene, and on adding water (β)-hexyl alcohol is ppd.

Hexylene CMe_2:CMe_2. *Tetra-methyl-ethylene.* (73°). S.G. $^{\underline{0}}$ ·712. Formed by the action of alcoholic KOH on CMe_2ᏢrI (Jawein, *A.* 195, 253; Pawloff, *A.* 196, 124; Rizza, *J. R.* 1882, 99; *C. J.* 42, 491). Formed also, together with a heptylene, by heating CMe_2:CHMe with PbO and MeI for eight hours at 225° (Eltekoff, *J. R.* 14, 380). Forms a dibromide $C_6H_{12}Br_2$ [169°]. A 10 p.c. solution of CrO_3 completely oxidises tetra-methyl-ethylene to acetone. Butlerow (*J. R.* 11, 219) also obtained tri-methyl-acetic acid by oxidation. H_2SO_4 (2 vols.), mixed with water (1 vol.), polymerises it to $C_{12}H_{24}$ at 60°.

Hexylene $CMe_3.CH:CH_2$. (70°). From pinacolin iodide by distillation with water (Friedel a. Silva, *C. R.* 76, 226). Forms a crystalline dibromide.

Hexylene CHMe:CMeEt. (70°). S.G. ·712; $^{\underline{19}}$ ·698. C.E. ·00116. From $CMeEt_2I$ and alcoholic KOH (Tschaikowsky, *J.* 1872, 350; Jawein, *A.* 195, 255) It is also a product of the action of zinc and glacial acetic acid on $CH_3.CH_2$.CHMe.CHMeI (Wislicenus, *A.* 219, 313). Combines with HI forming $CMeEt_2I$. Chromic acid oxidises it with difficulty forming acetic acid and a small quantity of a ketone. By agitating the hexylene (1 vol.) with (2 vols. of) a mixture of H_2SO_4 (2 pts.) and water (1 pt.) at 0° until it is dissolved, and subsequently exposing the solution to the air, there is formed an oily dodecylene $C_{12}H_{24}$ (196°–199°); S.G. $\underline{0}$ ·809; $\underline{19}$ ·798. C.E. ·00080.

Hexylene $CHEt{:}CMe_2$. (66°). S.G. $\underline{0}$ ·702; $\underline{12}$ ·687. C.E. ·00117. From CMe_2PrI and alcoholic KOH (Jawein, *A.* 195, 255). Chromic acid oxidises it to acetic and propionic acids and acetone. Polymerised in the same manner as the preceding body, forming a dodecylene $C_{12}H_{24}$ (195°). S.G. $\underline{0}$ ·795; $\underline{12}$ ·786. C.E. ·00065.

Hexylene C_6H_{12}. (60°–70°). Obtained by distilling fusel oil with $ZnCl_2$ (Wurtz, *A.* 128, 228). Forms a dibromide $C_6H_{12}Br_2$ (190°–200°).

Hexylene C_6H_{12}. (65°). S.G. $\underline{0}$ ·694. Obtained by distilling the lime-soap obtained from whale oil (Warren a. Storer, *Z.* 1868, 228).

Hexylene C_6H_{12}. (67°–70°). In oil of resin (Renard, *A. Ch.* [6] 1, 227).

Hexylene C_6H_{12}. (70°–80°). *Dipropylene.* From propylene bromide, zinc, and HOAc (Prunier, *C. R.* 76, 98).

References.—Bromo- and Di-chloro-hexylene.

Di-hexylene *v.* Dodecylene.

HEXYLENE ALCOHOL *v.* Di-oxy-hexane.

HEXYLENE CHLORHYDRIN *v.* Chloro-hexyl alcohol.

HEXYLENE GLYCOL *v.* Di-oxy-hexane and Pinacone.

HEXYLENE IODIDE *v.* Di-iodo-hexane.

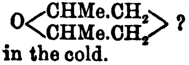
HEXYLENE OXIDE $C_6H_{10}O$ *i.e.*

$O\langle\begin{smallmatrix}CMe_2\\CMe_2\end{smallmatrix}\rangle$. (96°). Formed from $CMe_2{:}CMe_2$ by conversion into $CMe_2Cl.CMe_2OH$ [55°] and treatment of this chloro-hexyl alcohol with KOH (Eltekoff, *Bl.* [2] 40, 23; *J. R.* 1882, 355). Combines with water with evolution of heat, the product being pinacone.

Hexylene oxide $C_6H_{10}O$ *i.e.*

$O\langle\begin{smallmatrix}CHMe\\CHPr\end{smallmatrix}\rangle$. (110°). S.G. $\underline{13{\cdot}8}$ ·8236. From (β)-hexylene $Pr.CH{:}CHMe$, by successive treatment with ClOH and conc. KOHAq (Eltekoff, *Bl.* [2] 40, 23; Henry, *A. Ch.* [5] 29, 553). Liquid. Does not combine with cold water, but at 100° it forms di-oxy-hexane $PrCH(OH).CH(OH)Me$. A mixture of H_2SO_4 and HNO_3 forms the nitrate $C_6H_{12}(NO_3)_2$.

Hexylene oxide $C_6H_{10}O$ *i.e.*

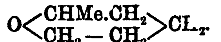


$O\langle\begin{smallmatrix}CHMe.CH_2\\CHMe.CH_2\end{smallmatrix}\rangle$? (93°). S.G. $\underline{0}$ ·837. S. 7 in the cold.

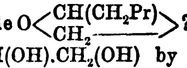
Formation.—1. Together with hexenyl alcohol, by the action of Ag_2O on the di-iodo-hydride of diallyl (di-iodo-hexane) (Wurtz, *A. Ch.* [4] 3, 175).—2. By treating diallyl with H_2SO_4 and distilling with water (Jekyll, *Z.* 1871, 36).

Properties.—Liquid, does not react with $NaHSO_3$, hydroxylamine, ammoniacal $AgNO_3$, cold HClAq, or water at 170°. Does not ppt. a solution of $MgCl_2$. Sodium-amalgam does not reduce it.

Reactions.—1. HClAq at 150° forms a chloro-hexyl alcohol (170°–180°) (Béhal, *Bl.* [2] 48, 43; *A. Ch.* [6] 16, 200) and, finally, di-chloro-hexane. 2. Fuming HIAq at 100° forms *sec*-hexyl iodide. 3. *Chromic acid mixture* oxidises it to CO_2 and acetic acid.—4. Excess of *bromine* forms di-bromo-hexane and an aldehyde.



Hexylene-δ-oxide $O\langle\begin{smallmatrix}CHMe.CH_2\\CH_2-CH_2\end{smallmatrix}\rangle CL_2$. (104° at 720 mm.). S.G. $\underline{0}$ ·8739. Very mobile colourless liquid of strong ethereal smell. V. sol. alcohol and ether, sl. sol. water. Volatile with steam. Prepared by heating the glycol with 3 pts. of H_2SO_4 (65 p.c.) at 100°. It is not affected by heating with water or with aqueous or alcoholic NH_3 even at 200°. By boiling with dilute HCl it is converted into the chlorhydrin (Lipp, *B.* 18, 3283).



Hexylene oxide $O\langle\begin{smallmatrix}CH(CH_2Pr)\\CH_2\text{———}\end{smallmatrix}\rangle$? (115°). From $Pr.CH_2.CH(OH).CH_2(OH)$ by conversion into the chlorhydrin (chloro-hexyl alcohol) and treatment of the latter with KOH (Wurtz, *A.Ch.* [4] 3, 184).

Hexylene oxide? $C_6H_{10}O$. (185°). From PrPr by conversion into $C_6H_{12}Br_2$ and treatment of this di-bromo-hexane with AgOAc and KOH successively (Silva, *Bl.* [2] 19, 147).

HEXYLENIC ACID *v.* Hexenoic acid.

HEXYL-GLYCERIN *v.* Tri-oxy-hexane.

HEXYL-GLYCOL *v.* Di-oxy-hexane.

HEXYL-GLYOXALINE $C_9H_{16}N_2$ *i.e.* $C_3H_3(C_6H_{13})N_2$. *Glyoxal-œnanthyline.* [84°] (Radziszewski, *B.* 16, 748); [51°] (Karcz, *M.* 8, 218). (295°). Prepared by the action of glyoxal on heptoic aldehyde-ammonia (œnanthol-ammonia) in alcoholic solution (R.), or by passing NH_3 into a mixture of glyoxal and heptoic aldehyde (K.). Thin glistening needles; sol. alcohol, sl. sol. ether, insol. water. Karcz attributes the difference in the melting-point, as observed by himself and by Radziszewski, to the existence of two allotropic forms of the hexyl-glyoxaline. MeI gives $C_3H_2Me(C_6H_{13})N_2$ (262°); EtI and PrI act in like manner.

Salts.—BHCl: colourless deliquescent needles.—B′HBr.—$B'_2H_2C_2O_4$. [121°].

HEXYL HEPTADECYL KETONE $C_{24}H_{18}O$ *i.e.* $C_6H_{13}.CO.C_{17}H_{35}$. (243°) at 10 mm. Formed by distilling barium stearate with barium heptoate (Krafft, *B.* 15, 1718).

HEXYL HYDRIDE *v.* Hexane.

***n*-HEXYL IODIDE** $C_6H_{13}I$ *i.e.* $Pr.CH_2.CH_2.CH_2I$. (177°) (Dobriner, *A.* 243, 27); (179·5°) (Franchimont a. Zincke, *A.* 163, 196); (182° cor.) (Lieben a. Janecek, *A.* 187, 138). S.G. $\frac{0}{0}$ 1·4661 (D.); $\underline{17{\cdot}5}$ 1·412 (F. a. Z.); $\underline{0}$ 1·461 (L. a. J.). C.E. (0°–10°) ·00095 (D.). S.V. 173·8. Prepared from *n*-hexyl alcohol and HI.

Hexyl iodide $C_6H_{13}I$. (172°–175°). S.G. $\underline{12}$ 1·43. Obtained from petroleum hexane *viâ* hexyl alcohol (Pelouze a. Cahours, *C. R.* 54, 1241).

Sec-**hexyl iodide** $C_6H_{13}I$ *i.e.* $Pr.CH_2.CHI.CH_3$. (β)-*hexyl-iodide.* (168° i.V.). S.G. $\underline{0}$ 1·45; $\frac{15}{15}$ 1·4269; $\frac{25}{25}$ 1·4163 (Perkin, *C. J.* 45, 463). C.E. (0°–50°) ·00092. M.M. 14·229 at 23·9°.

Formation.—1. By boiling mannite or dulcite with a great excess of conc. HIAq (Wanklyn a. Erlenmeyer, *Z.* 1861, 606; 1862, 641).—2. By the action of HI on (β)-hexylene obtained by treating the di hydro-di-iodide of diallyl with sodium (Wurtz, *A.* 132, 306).—3. From hexylene oxide (93°) and HI (Jekyll, *C. N.* 22, 221).

Preparation.—1. Mannite (24 g.) is distilled with aqueous HI (300 c.c. boiling at 126°) and clear phosphorus in a current of CO_2. The yield is nearly the theoretical (E. a. W.).—2. Iodine (75 g.) and water (130 g.) are treated, in an atmosphere of CO_2, with clear phosphorus until colourless; mannite (25 g.) is then added, and the mixture distilled in a current of CO_2 (Domac, *M.* 2, 310; *cf.* Hecht, *A.* 165, 148).—3. A mixture of mannite (200 g.) and red phosphorus (100 g.) is added slowly to HIAq (500 g. of 57 p.c.), and the mixture distilled in a current of CO_2 (Hecht, *A.* 209, 311).—4. A good yield is obtained by distilling mannite with fuming HIAq and a little amorphous phosphorus (Schorlemmer, *T.* 171, 452).

Properties. — Liquid, smells like isoamyl iodide.

Reactions.—1. *Alcoholic potash* gives (β)-hexylene.—2. By heating with *water* at 190° it gives hexylene. By boiling for a long time with a large excess of water (45 pts.) *sec*-hexyl alcohol is the chief product, hexylene being also formed (Niederist, *A.* 196, 351).—3. With moist Ag_2O, with *zinc* and water, with zinc and alcohol, with silver oxalate, with sodium, with mercury, and with $ZnMe_2$, it yields hexylene.—4. When (β)-hexyl iodide (100 g.) is heated with iodine (25 g.) for 5 hours to 256° it yields hexane, HI, a little MeI, and a combustible gas (Rayman a. Preis, *A.* 223, 322).—5. *Chloride of iodine* at 240° gives hexa-chloro-benzene, CCl_4, C_2Cl_6, and C_4Cl_6 (Krafft, *B.* 9, 1085).—6. *Chromic acid mixture* oxidises it to acetic and butyric acids (Hecht, *B.* 11, 1421).

Sec-**hexyl iodide** $C_6H_{13}I$ *i.e.* Pr.CHEtI (?) *Di-ethylated ethyl iodide.* (100°) at 70 mm. From di-chloro-di-ethyl oxide $CH_2Cl.CHCl.OEt$ *viâ* $CH_2Et.CHEt.OEt$ (Lieben, *A.* 178, 18). Probably identical with the following.

Sec-**hexyl iodide** Pr.CHEtI. (165°). From the alcohol and HI (Oechsner de Coninck, *Bl.* [2] 25, 9).

Sec-**hexyl iodide** CHMeEt.CHMeI. From the corresponding hexyl alcohol and HI (Wislicenus, *A.* 219, 310). Liquid; decomposed on distillation. Zinc and acetic acid reduce it to $CHMeEt.CH_2Me$, a hexylene, and a dodecylene, some methyl-di-ethyl-carbinol being also formed.

Sec-**hexyl iodide** $(CH_3)_3C.CHMeI$. (142°). S.G. $^{\underline{0}}$ 1·474; $^{\underline{25}}$ 1·442. From the corresponding alcohol and PI_2 (Friedel a. Silva, *C. R.* 76, 226). Partially split up on distillation with water into HI and a hexylene (70°).

Hexyl iodide $C_6H_{13}I$. (c. 150°). Formed by combination of HI with the hexylene derived from fusel oil (Wurtz, *A.* 128, 228).

Tert-**hexyl iodide** $CMeEt_2I$. (142°). Formed by leaving equal volumes of methyl-di-ethyl-carbinol and fuming HIAq to stand in the cold. Formed also from $CH_3.CH:CMeEt$ and HI (Wislicenus, *A.* 219, 318; Tschaikowsky, *J.* 1872, 350; Reformatsky, *J. pr.* [2] 36, 340). Liquid; partially decomposed on distillation.

Tert-**hexyl iodide** CMe_2PrI. (142°). Formed by the action of HI on di-methyl-propyl-carbinol or on $CMe_2:CHEt$ (Jawein, *A.* 195, 254).

Tert-**hexyl iodide** CMe_2PrI. (142°). S.G. $^{\underline{0}}$ 1·394; $^{\underline{12}}$ 1·373. From $CMe_2:CMe_2$ and HI (Pawloff, *A.* 196, 125). Solidifies at 0° (Kaschirski, *C. C.* 1881, 278). Slightly decomposed by distillation.

DI-HEXYL KETONE $C_{13}H_{26}O$ *i.e.* $(C_6H_{13})_2CO$. [30°]. (264° cor.). S.G. $^{\underline{30}}$ ·825. Formed by the dry distillation of calcium heptoate (œnanthoate) (Uslar a. Seekamp, *A.* 108, 179). Large colourless laminæ (from alcohol).

Sec-**HEXYL-MALONIC ACID** $C_6H_{13}.CH(CO_2H)_2$. [c. 86°]. From the ether by saponification. Nodules, v. sol. water, alcohol, and ether.

Ethyl ether Et_2A''. (251°). From sodium malonic ether and (β)-hexyl iodide (Lundahl, *B.* 16, 789).

n-(?)-**HEXYL MERCAPTAN** $C_6H_{13}SH$. (145°–148°). From petroleum hexane by conversion into hexyl chloride followed by treatment with KSH (Pelouze a. Cahours, *A.* 124, 291).

Sec-**hexyl mercaptan** $Pr.CH_2.CHMe.SH$. (142°). S.G. $^{\underline{0}}$ ·886. From (β)-hexyl iodide and conc. alcoholic KSH (Wanklyn a. Erlenmeyer, *A.* 135, 150). Colourless oil, with unpleasant smell.—$Hg(SC_6H_{13})_2$. Liquid. S.G. $^{\underline{0}}$ 1·650.

HEXYL-NITROUS ACID so-called. $C_6H_{12}N_2O_4$. (212°). S.G. $\frac{0}{4}$ 1·1381. Formed by the action of HNO_3 on methyl-hexyl ketone (Chancel, *C. R.* 94, 399; 100, 601). Oil, slightly decomposed by distillation. May be reduced to *n*-hexoic acid.—$C_6H_{11}KN_2O_4$: slender yellow plates (from water); sl. sol. water. Decomposes without detonation when heated. The silver salt is a similar body.

DI-*sec*-HEXYL OXIDE $(C_6H_{13})_2O$. (204°–209°). Formed, together with a hexylene and hexyl alcohol, by the action of moist Ag_2O on (β)-hexyl iodide (Erlenmeyer a. Wanklyn, *Z.* 1863, 274). Thick yellowish oil.

HEXYL-PARACONIC ACID *v.* OXY-HEPTYL-SUCCINIC ACID.

HEXYL PENTADECYL KETONE $C_{22}H_{44}O$ *i.e.* $C_6H_{13}.CO.C_{15}H_{31}$. (231°) at 10 mm. Formed by distilling a mixture of barium palmitate and barium heptoate (Krafft, *B.* 15, 1718).

HEXYL SULPHIDE $(C_6H_{13})_2S$. (230°). From petroleum hexane *viâ* hexyl chloride (Pelouze a. Cahours, *A.* 124, 291). Oil.

HEXYL SULPHOCYANIDE $C_6H_{13}SCy$. (215°–220°). S.G. $^{\underline{12}}$ ·922. Formed by heating potassium sulphocyanide at 100° with an alcoholic solution of hexyl chloride derived from petroleum (Pelouze a. Cahours, *A. Ch.* [4] 1, 5). Fetid liquid.

Sec-**hexyl sulphocyanide** $Pr.CH_2.CHMe.SCy$. (207°). Prepared by boiling equal parts of (β)-hexyl iodide with potassium sulphocyanide dissolved in alcohol (Uppenkamp, *B.* 8, 55). Oil, with alliaceous odour.

n-**HEXYL THIOCARBIMIDE** $C_6H_{13}NCS$. (212°). Formed by distilling cupric *n*-hexyl-di-thio-carbamate with steam (Frentzel, *B.* 16, 746). Pungent oil.

Sec-**hexyl thiocarbimide** $Pr.CH_2.CHMeNCS$. (198°). S.G. ·92. From (β)-hexylamine by boiling with CS_2 and alcohol, evaporating, and heating the residue with a solution of mercuric chloride (Uppenkamp. *B.* 8, 56). Oil. Converted by hot conc. H_2SO_4 into (β)-hexylamine.

n-**HEXYL THIO-UREA** $C_7H_{16}N_2S$ *i.e.* $CS(NH_2)(NH.C_6H_{13})$. [83°]. From *n*-hexyl thiocarbimide and alcoholic NH_3 (Frentzel, *B.* 16, 746). White plates (from alcohol).

Di-*n*-hexyl thio-urea $CS(NHC_6H_{13})_2$. [40°]. Obtained by heating *n*-hexylammonium *n*-hexyl-di-thio-carbamate (F.). White plates (from alcohol).

HEXYL-TRIDECYL-KETONE $C_{20}H_{40}O$ *i.e.* $C_6H_{13}.CO.C_{13}H_{27}$. (210° at 11 mm.). Formed by distilling a mixture of barium heptoate and barium myristate (Krafft, *B.* 15, 1717).

HEXYL-UREA. *Heptoyl derivative* $C_6H_{13}NH.CO.NH.CO.C_6H_{13}$. [97°]. Formed by the action of KOH on a mixture of the amide of heptoic (œnanthoic) acid and bromine (Hofmann, *B.* 15, 759). Pearly plates; insol. water.

***Sec*-hexyl-urea** $NH_2.CO.NH.CHMe.CH_2Pr$. [127°]. (c. 220°). From (β)-hexyl iodide and silver cyanate, the resulting thiocarbimide being decomposed by shaking with aqueous ammonia (Chydenius, *Bl.* [2] 7, 481). Slender needles (from water); v. sol. water, alcohol, and ether. Not decomposed by conc. KOHAq below 200°.

HIPPARAFFIN *v. Dibenzoyl derivative* of METHYLENE-DIAMINE.

HIPPURIC ACID $C_9H_9NO_3$ *i.e.* $NHBz.CH_2.CO_2H$. *Benzoyl-glycocoll. Benzoyl-amido-acetic acid. Benzamido-acetic acid.* Mol. w. 179. [187°]. S.G. 1·308 (Schabus, *Sitz. W.* 1850, 211). S. ·17 at 0°. S. (isoamyl alcohol) 2 at 9°; 33 on boiling (Campani, *B.* 11, 1247).

Occurrence.—1. In the urine of herbivorous animals and in small quantity (c. 1 g. daily) in that of man (Liebig, *A.* 12, 20; Henneberg, Stohmann a. Rautenberg, *A.* 124, 181; Bence Jones, *C. J.* 15, 81; Thudichum, *C. J.* 17, 55; Weismann, *J. pr.* 74, 106; Wreden, *J. pr.* 77, 446; Hofmeister, *L. V.* 14, 458; Wildt, *B.* 6, 1410; Kraut, *C. C.* 1858, 831; Loew, *J. pr.* [2] 19, 309; Stadelmann, *J.* 1879, 982; Schwarz, *A.* 54, 32; Weiske, Wildt a. Pfeiffer, *B.* 6, 1410; Hallwachs, *A.* 106, 164; E. Salkowski, *B.* 11, 500; Weyl a. Aurep, *B.* 13, 1092; Garrod, *Pr.* 35, 63; 37, 148; Minkowski, *J.* 1883, 1440).—2. In the blood of oxen (Verdeil a. Dollfus, *A.* 74, 214).—3. In the human epidermis in ichthyosis (Schlossberger, *A.* 93, 347).

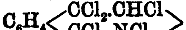
Formation.—1. Excreted by the animal organism after introduction of benzoic acid (Bouis a. Ure, *B. J.* 22, 567; Ure, *J. Ph.* 27, 646; Keller, *A.* 43, 108; Garrod, *P. M.* [3] 20, 501). Quinic acid (Lautemann, *A.* 125, 9), cinnamic acid (Erdmann a. Marchand, *B. J.* 23, 646) toluene (Naunyn a. Schultzen, *Z.* 1868, 29), and phenyl-propionic acid also yield hippuric acid when passed through the animal organism. Since phenyl-propionic acid is produced by the pancreatic fermentation of proteïds, hippuric acid is, at any rate in part, due to the decomposition of proteïds (E. a. H. Salkowski, *B.* 12, 654; Baumann, *H.* 10, 131).—2. From benzoyl chloride and zinc glycocoll or from glycocoll and benzoic acid at 100° (Dessaignes, *C. R.* 37, 251). The yield is very bad.—3. From chloro-acetic acid and benzamide (Jazukowitch, *Bl.* [2] 8, 361). The yield is bad.—4. By heating glycocoll with benzoic anhydride (Curtius, *B.* 17, 1662).—4. From silver glycocoll and BzCl (Curtius, *J. pr.* [2] 26, 170).—5. By adding benzoyl chloride to an aqueous solution of glycocoll and making alkaline with NaOH (Baum, *B.* 19, 502).

Preparation.—1. The urine of horses or cows is boiled with addition of some milk of lime, filtered, neutralised by HCl, evaporated, acidified by HCl and allowed to stand. Hippuric acid is then deposited as a yellowish-brown pp. (Gregory, *A.* 63, 125; *cf.* Riley, *C. J.* 5, 97). When horses' urine is quickly evaporated the hippuric acid is partly converted into benzoic acid. Crude hippuric acid, obtained as above, is then mixed with rather less water than will dissolve it at 100°. The liquid is then heated to 100° and chlorine passed in until the unpleasant odour of the crude product has disappeared. The liquid is filtered hot, and the acid that separates on cooling is subjected a second time to the same treatment, chlorine being passed in this time until the liquid is bright yellow. The yield is 65 p.c. of the crude acid (T. Curtius, *J. pr.* [2] 26, 149; *cf.* Dauber, *A.* 74, 202; Conrad, *J. pr.* [2] 15, 242; Gössmann, *A.* 99, 374; Schwarz, *A.* 54, 29; Hansen, *J. Th.* 1881, 117).—2. Silver glycocoll is suspended in a mixture of benzene (1 vol.) and ether (2 vols.) and benzoyl chloride is added. On warming AgCl is formed together with several acids. The liquid is evaporated and benzoic acid removed by solution in ether. Three nitrogenous acids remain. They are dissolved in NaOH, reppd. by HCl, dried and extracted thoroughly with chloroform. This dissolves the hippuric acid, which is present in greatest quantity. One of the remaining acids is hippuryl-glycocoll (*q. v.*) (Curtius, *J. pr.* [2] 26, 168). The other has the formula $C_{10}H_{12}N_2O_4$. Both these acids split up with formation of hippuric acid when they are heated with dilute HCl.

Properties.—Crystallises from water in very large trimetric prisms; $a:b:c = \cdot974:1:1\cdot161:1$. Has a slightly bitter taste, and strongly reddens litmus. Sl. sol. cold, v. sol. boiling, water. V. sol. hot alcohol, v. sl. sol. ether. Less soluble in water containing HCl, and hence is ppd. on adding a considerable excess of HCl to cow's urine. Dissolves readily in water containing sodium phosphate, the solution becoming acid; in this respect it resembles uric acid. Insol. benzene, CS_2, and cold chloroform. Sol. EtOAc. $FeCl_3$ forms, in a dilute solution of an alkaline hippurate, a cream-coloured pp. of basic ferric hippurate $FeA'_3Fe_2O_3$ 1½aq, which is moderately soluble in excess of ferric chloride (E. Salkowski, *Z.* [2] 4, 313).

Estimation in urine.—1. Recently calcined MgO is added to 1 litre of urine, the liquid is concentrated, acidified with HCl and extracted with ether (A. W. Blyth, *Pr.* 37, 50).—2. 250 c.c. of urine are evaporated to 80 c.c., 4 g. of sodium phosphate are added, and the evaporation continued to syrupy consistence. Plaster of Paris is then added till the mass can be powdered, after which it is extracted first with light petroleum and then with ether. The ethereal extract is evaporated, and the hippuric acid decolourised with charcoal, crystallised from water, and weighed (Voelker, *Fr.* 26, 402).

Reactions.—1. On *heating* to 240° hippuric acid begins to boil, giving off benzoic acid and benzonitrile (Gössmann, *A.* 100, 69; Limpricht a. von Uslar, *A.* 88, 133).—2. Boiling aqueous *hydrochloric acid* splits it up into benzoic acid and glycocoll. Dilute H_2SO_4, HNO_3, and oxalic acid behave in like manner.—3. By boiling for half an hour with aqueous *caustic potash* it is resolved into glycocoll and potassium benzoate. Boiling milk of lime does not effect its hydrolysis.—4. Some ferments hydrolyse hippuric acid (Buchner, *A.* 78, 203).—5. *Nitrous acid* converts it into the benzoyl derivative of glycollic acid, with evolution of nitrogen.—6. When boiled with NaOBr and an excess of alkali for a long time, a bright-red powder is deposited on cooling (Denigès, *C. R.* 107, 662).—7. HCl and $KClO_3$ form chloro- and di-chloro-hippuric acids (Otto, *A.* 122, 129).—8. A cold mixture of H_2SO_4 and HNO_3 forms nitro-hippuric acid.—9. SO_3 gives sulpho-hippuric acid.—10. *Chlorine* passed into a solution of hippuric acid in dilute KOH forms benzoyl-glycollic acid, nitrogen being evolved (Gössmann).—11. The prolonged action of PCl_5 forms $C_9H_5NCl_6$ probably hexa-chloro-isoquinoline tetrahydride



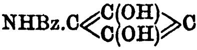
$C_6H_4<\begin{matrix}CCl_2.CHCl\\CCl_2.NCl\end{matrix}>$

[184°] (Rügheimer, *B.* 19, 1169). This body crystallises in plates. By distilling hippuric acid (1 mol.) with PCl_5 (2 mols.) Schwanert (*A.* 112, 59) obtained C_9H_6ClNO [50°] (220°) and $C_9H_5Cl_2NO$.—12. Boiling with MnO_2 and very dilute H_2SO_4 forms benzoic acid, NH_3, and CO_2. 13. When heated with PbO_2 and excess of HNO_3 or H_2SO_4 the product is the di-benzoyl derivative of methylene-diamine (hipparaffin).—14. Boiling with water and PbO_2, with addition of only enough H_2SO_4 to combine with the lead, produces benzamide (Fehling, *A.* 28, 48; Schwarz, *A.* 75, 190).—15. *Ozone* oxidises it to benzoic and acetic acids (Gorup-Besanez, *A.* 125, 217).—16. By boiling with $KMnO_4$ and KOH all the nitrogen is expelled as NH_3 (Wanklyn a. Chapman, *C. J.* 21, 161).—17. A concentrated aqueous solution of $ZnCl_2$ at 120° forms benzoic acid and glycocoll. Distillation with dry $ZnCl_2$ gives benzonitrile (Gössmann, *A.* 100, 69).—18. *Sodium amalgam* added to an alkaline solution of hippuric acid forms 'hydrobenzuric acid' $C_{18}H_{24}N_2O_6$ and 'hydrobenzyluric acid' $C_{16}H_{21}NO_4$; the latter dissolves in ether, the former does not (Otto, *A.* 134, 303). Both acids give glycocoll when boiled with alkalis; the latter forms also benzyl alcohol and hydrobenzoic acid. When hydrobenzyluric acid is heated with alkalis and at the same time exposed to the air, there is formed 'hydroxybenzyluric acid' $C_{16}H_{21}NO_5$ [60°–70°], which when left in a desiccator over H_2SO_4 changes to an acid $C_{16}H_{19}NO_4$. 19. *Pyruvic acid* (6 g.) digested with sodium hippurate (11 g.) and Ac_2O (25 g.) at 100° forms a compound $C_{12}H_9NO_4$ which crystallises from petroleum in flat needles [157°], v. sol. alcohol, ether, and HOAc, insol. water. It seems to be an anhydride, for baryta forms the salt $C_{12}H_9BaNO_5$ 2aq (A. Hoffmann, *B.* 19, 2554).—20. By mixing hippuric acid with salicylic aldehyde and excess of Ac_2O and allowing the mixture to stand for some weeks there is formed a compound $C_{32}H_{24}N_2O_7$ [160°] (Plöchl a. Wolfram, *B.* 18, 1184). Rebuffat (*G.* 15, 527) by boiling sodium hippurate (62 g.) with salicylic aldehyde (40 g.) and Ac_2O (120 g.) obtained a compound $C_{16}H_{13}NO_4$ which crystallised from alcohol in canary-yellow prisms [136°], and is converted by hot aqueous (10 p.c.) KOH into benzoyl-imido-coumarin $C_{16}H_{11}NO_3$ [171°] and an acid $C_{16}H_{13}NO_4$ [185°].—21. *Phthalic anhydride* yields a compound $C_{34}H_{18}N_2O_8$ (E. Erlenmeyer, jun., *B.* 22, 792).

Salts.—$NH_4A'HA'aq$: formed even in presence of excess of NH_3. Square-based prisms with four-sided summits, v. sol. water and alcohol, sl. sol. ether. Gyrates when thrown on the surface of water.—KA′ aq: prisms, sol. water and alcohol.—KA′HA′ aq.—NaA′ ½aq: v. sol. hot water and alcohol, sl. sol. ether.—BaA'_2 aq: prisms, sol. water; forms with barium benzoate the double salt $BaA'_2Ba(OBz)_2$ 5aq.—CaA'_2 3aq: trimetric prisms. S. 5·6 in the cold; 17 at 100°. S.G. 1·32.—SrA'_2 5aq: sl. sol. cold water and alcohol.—MgA′ 5aq: white nodules, sol. water.—ZnA'_2 5aq: laminæ. S. (of ZnA'_2) 1·8 at 17·5°; 25 at 100°.—CuA'_2 3aq: azure prisms, sl. sol. cold water.—PbA'_2 2aq: silky needles, deposited on diluting a boiling solution.—PbA'_2 3aq: broad laminæ.—CoA'_2 5aq: rose-coloured needles.—NiA'_2 5aq: sl. sol. cold, m. sol. boiling water and boiling alcohol, insol. ether.—CeA'_3 4½aq (Czudnovitch, *J. pr.* 82, 277).—LaA'_3 4½aq (Czudnovitch, *J. pr.* 80, 31).—FeA'_3 (Wreden, *C. C.* 1859, 552).—$Fe(OH)A'_2$ (Salkowski, *J. pr.* 102, 327; *cf.* Putz, *J.* 1877, 795).—AgA′ ½aq: may be crystallised from water.

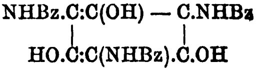
Methyl ether MeA′. [80·5°]. S. ·85 in the cold; 1·3 at 30°. Formed by passing HCl into a solution of hippuric acid in methyl alcohol at 60° (Jacquemin a. Schlagdenhauffen, *C. R.* 45, 1011; Conrad, *J. pr.* [2] 15, 247; Campani a. Bizzari, *G.* 10, 260). White needles. Decomposed at 250°, giving off NH_3 and benzonitrile.

Ethyl ether EtA′. [60°]. S.G. ^{22} 1·043. Formed by passing HCl into a boiling alcoholic solution of hippuric acid (Stenhouse, *A.* 31, 148), or by heating amido-acetic ether with benzoic anhydride (Curtius, *B.* 17, 1662). White needles, sl. sol. hot water, v. sol. ether. When hippuric ether (5 pts.) is heated with dry NaOEt (1 pt.) to 160°, alcohol distils over, and there is left a mixture of two sodium salts, which may be separated by water. The less soluble salt, when decomposed by HCl, yields the di-benzoyl-derivative of di-oxy-di-amido-tetramethylene;



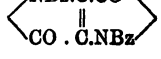
$NHBz.C<\begin{matrix}C(OH)\\C(OH)\end{matrix}>C.NHBz$

[138°]; the more soluble salt yields the tri-benzoyl derivative of tri-amido-phloroglucin



$$\begin{matrix}NHBz.C{:}C(OH) & - & C.NHBz\\ | & & |\\ HO.C{:}C(NHBz) & . & C.OH\end{matrix}$$

[153·5°–158·5°] (Rügheimer, *B.* 21, 3325). When hippuric ether is heated with PCl_5 for eight hours at 160°, and the product poured into alcohol, 'hippuroflavin' separates. It crystallises from hot HOAc in small yellow crystals, and partially decomposes, without melting, at 300°. Hippuroflavin is v. sl. sol. glacial HOAc, and almost insol. water, alcohol, and ether. It has perhaps the constitution



$$<\begin{matrix}NBz.C.CO\\ \|\\ CO\,.\,C.NBz\end{matrix}>$$

(Rügheimer, *B.* 21, 3321).

n-Butyl ether $PrCH_2.A'$. [41°]. From silver hippurate and *n*-butyl iodide (C. a. B.). Iridescent prisms, insol. water, sol. alcohol, ether, and chloroform.

Isobutyl ether $PrCH_2A'$. [46°]. From AgA′ and isobutyl iodide in presence of isobutyl alcohol (C. a. B.). Iridescent prisms. Decomposed by damp air.

Isoamyl ether $C_5H_{11}A'$. [28°].

Benzyl ether $PhCH_2A'$. [86°]. From AgA' and benzyl bromide (Del Zanna a. Guareschi, *Atti Real. Istit. Veneto* [5] 6). Silky needles. Converted by HNO_3 into benzoic aldehyde.

Amide $C_9H_8NO_2NH_2$. [183°]. S. 1 in the cold. Formed by the prolonged action of aqueous ammonia on methyl hippurate (Jacquemin a. Schlagdenhauffen, *C. R.* 45, 1011). Formed also by heating hippuric acid in a current of NH_3 at 160° (Conrad, *J pr.* [2] 15, 248). Small thick crystals, v. sl. sol. cold water, alcohol, and ether. Forms an unstable compound with HCl.

Ureide $NHBz.CH_2.CO.NH.CO.NH_2$. [216°]. Formed, together with another compound [189°], by heating ethyl hippurate with urea at 150° (Curtius, *B.* 16, 757); and by heating hippuric acid with alcoholic NH_3 at 220° (Pellizzari, *C. C.* 1888, 1350). Silvery plates; decomposed by boiling dilute acids into hippuric acid and urea. Split up by alcoholic NH_3 at 260°, giving benzamide and EtOBz.

References.—Amido-, Bromo-, Chloro-, Iodo-, Nitro-, Oxy-, and Sulpho-hippuric acid.

HIPPURYL-GLYCOCOLL $C_{11}H_{12}N_2O_4$ *i.e.* $Bz.NH.CH_2.CO.NH.CH_2.CO_2H$. [207°].

Preparation.—Silver glycocoll (40 g.), benzoyl chloride (15·5 g.), and benzene (200 c.c.) are heated together until HCl begins to come off. The product is evaporated, extracted with ether, then with NaOH. The mixed acids are ppd. by HCl, dried and exhausted with alcohol. The alcoholic extract leaves on evaporation a mixture of hippuric acid and hippuryl glycocoll. The greater part of the former may be removed by chloroform, and the hippuryl glycocoll is then purified by recrystallising 20 or 30 times from 30 p.c. alcohol (Curtius, *J. pr.* [2] 26, 170). In this reaction benzoyl chloride acting on silver glycocoll forms silver chloride and hippuric acid. This hippuric acid acts upon benzoyl chloride forming benzoic acid and hippuryl chloride, which then attacks silver glycocoll, forming silver chloride and hippuryl-glycocoll.

Properties.—Satiny trimetric plates (from water). The crystals are small, and feel fatty. Insol. ether, $CHCl_3$, benzene, and CS_2 in the cold, but sl. sol. these solvents when boiling. Readily sol. boiling dilute (30 p.c.) alcohol.

Reactions.—1. Boiled with HCl or KOH it gives glycocoll (2 equivalents) and benzoic acid (1 equivalent).—2. At 150° in a sealed tube with an aqueous solution containing the calculated quantity of HCl it splits up into glycocoll and hippuric acid.

Salts.—AgA': white crystalline pp., sol. hot water without reduction.—TlA': six-sided tablets.—BaA'_2 5aq (?). Little plates.—CuA_2' $3\frac{1}{2}$aq: trimetric prisms.—ZnA'_2 $1\frac{1}{2}$aq.

Ethyl ether EtA'. [117°]. Large needles (from water).

Amide $BzNH.CH_2CO.NH.CH_2CO.NH_2$. [202°]. Forms an unstable compound with HCl, which is at once resolved by water into its constituents.

HISTO-HÆMATINS *v.* Muscle.

HOFMANN'S VIOLET *v.* Penta-methyl-tri-amido-di-phenyl-tolyl-carbinol.

HOMO-ANISIC ACID *v. Methyl derivative* of Oxytoluic acid.

HOMO-BENZ-AMIDOXIM *v.* Tolu-amidoxim.

HOMO-CINCHONIDINE *v.* Cinchona bases.

HOMO-FERULIC ACID *v. m-Methyl derivative* of (4:3:1)-Di-oxy-phenyl-crotonic acid.

HOMOLOGOUS SERIES. A series of closely related compounds of which the molecules differ from one another by CH_2 or a multiple thereof. Homology is usually the result either (*a*) of the introduction of one or more methyl radicles in place of the equivalent quantity of hydrogen, or (*b*) of the insertion of a methylene group between two contiguous carbon atoms; thus benzoic acid $C_6H_5CO_2H$ is homologous with toluic acid $C_6H_4(CH_3).CO_2H$ in the first way, and with phenyl-acetic acid $C_6H_5.CH_2.CO_2H$ in the second way. In each homologous series there is a nearly constant difference in the properties of any two successive members of the series; this rule, however, does not apply to the difference between the first and second members, particularly where the first member does not contain CH_2. Although the alkyl derivatives of hydroxylic compounds differ from these compounds by a multiple of CH_2, and might therefore be considered homologous with the parent substance, yet as they belong to the group of ethers while their parents are acids or alcohols, this cannot be considered a case of true homology.

HOMO-NICOTINIC ACID *v.* Methyl-pyridine carboxylic acid.

HOMO-OXY-BENZOIC ACID *v.* Oxy-toluic acid.

HOMO-PHENACYL-ANILIDE *v.* ω-Phenyl amido-phenyl-ethyl ketone.

HOMO-PHTHALIC ACID *v.* Carboxy-phenyl acetic acid.

HOMO-PROTOCATECHUIC ACID *v.* Di-oxy-phenyl-acetic acid.

HOMOPYROCATECHIN, *Methyl ether* of, *v.* Creosol.

HOMO-PYRROLE *v.* Methyl-pyrrole.

HOMOQUININE *v.* Cinchona bases.

HOMOSALICYLIC ACID *v.* Oxy-toluic acid.

HOMO-VERATRIC ACID *v. Di-methyl derivative* of Di-oxy-phenyl-acetic acid.

HOPEÏNE $C_{18}H_{20}NO_4$ aq. S. ·125 at 15°. An alkaloid said to occur to the extent of ·15 p.c. in American wild hops, and of ·05 p.c. in English hops (Williamson, *J. Ph.* [5] 12, 460; *Chem. Zeit.* 10, 491). Brilliant white needles (from dilute alcohol). Narcotic. Sublimes partially below 160°. Slightly lævorotatory. Its dilute solutions are ppd. by alkalis, $PtCl_4$, $AuCl_3$, $HgCl_2$, picric acid, and tannin. According to Ladenburg (*B.* 19, 783), hopeine is identical with morphine, or is a mixture of morphine with an alkaloid that gives no colour with $FeCl_3$ or with H_2SO_4 and molybdic acid, and is insol. NaOHAq, v. sol. wet ether.

Lupuline. According to Griessmayer (*D. P. J.* 212, 67), when the aqueous extract of hops is distilled with lime or magnesia the distillate contains NH_3, trimethylamine, and an alkaloid lupuline. If the bases be converted into hydrochlorides, and these be treated with alcohol, NH_4Cl is left undissolved, while NMe_3HCl crystallises from the evaporated alcoholic solution, and the mother liquor contains lupuline hydrochloride. The base may be obtained by decomposing its hydrochloride with KOH and shaking with ether. It smells like coniine, has a cooling, but not bitter, taste, and gives the usual reactions of alkaloids. Conc. H_2SO_4 and potassium chromate give a violet colour. HNO_3 gives a yellow solution, becoming green or blue at its edges, and afterwards colourless.

HOP OIL. At the base of the membranous cones of the hop there is a bitter yellow powder called lupulin. This powder contains resin, wax, a tannin, and a bitter principle also called Lupulin (*q.v.*). When distilled with steam it yields hop oil, which consists of a terpene $C_{10}H_{16}$ (175°), and various compounds containing oxygen (Wagner, *D. P. J.* 128, 217; Personne, *J. Ph.* [3] 26, 241, 329; 27, 22; Kuhnemann, *C. C.* 1875, 573). One of the oxygenated constituents of oil of hops is converted into valeric acid by oxidation.

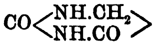
HUMIC ACID. The brown or black substance, or mixture of substances, produced by the decay of vegetable matter. The decomposition is promoted by heat, air, moisture, and by the presence of putrefying nitrogenous matter. Humic acid may be extracted from peaty soil by aqueous Na_2CO_3 and ppd. by HCl (Mulder, *A.* 36, 243; Detmer, *L. V.* 14, 248). Detmer assigned the formula $C_{60}H_{54}O_{27}$ to humic acid, and described it as amorphous, beginning to decompose at 145°, and requiring 8,333 parts of water at 6°, or 625 at 100°, to dissolve it. After drying it required 13,784 parts of boiling water for solution. It reddened litmus, expelled CO_2 from its salts, and formed the following amorphous salts. — $(NH_4)_6C_{60}H_{48}O_{27}$. S. 45. — $Ca_3(NH_4)_2C_{60}H_{46}O_{27}$. — $Fe_2(NH_4)_2C_{60}H_{46}O_{27}$. — $Ag_8C_{60}H_{46}O_{27}$. P. Thenard (*C. R.* 83, 375) described humic acid as $C_{24}H_{10}O_{10}$. 'Ulmic' acid prepared from brown peat is identical with humic acid. Crenic and apocrenic acids (*q. v.*) are, perhaps, products of oxidation of humic acid. Thenard obtained it by dissolving crude humic acid in potash, ppg. with a slight excess of HCl, washing the pp. well, and keeping the spongy mass at −14° for 24 hours. As the mass thaws the humic acid separates as a dense pp. Humic acid is not capable of converting atmospheric nitrogen into NH_3 (Prevost, *C. J.* 39, 370; *cf.* Simon, *Instit.* 1875, 133; Déhérain, *C. R.* 73, 1352). Lettenmayer (*B.* 7, 408) observed that a piece of rotten beech-wood which had fallen into a cleft of the tree protected from the rain, was covered with a brittle black layer readily soluble in cold water, and was composed of the K, Na, and NH_4 salts of an acid (? humic) containing 53·6 p.c. C and 4·9 p.c. H. When cane sugar is boiled for a long time with dilute HCl, HNO_3, or H_2SO_4, there is produced a substance greatly resembling humic acid, called Sacculmic acid (*q.v.*). A brown substance is formed by heating cellulose with water in a platinum tube at 200°; and brown substances are formed by the action of alkalis on glucose, cane-sugar, and many other substances. If all these brown bodies are included in the term humous substances, they may be subdivided into three groups: (*a*) those insol. alcohol and alkalis; (*b*) those insol. alcohol but sol. alkalis; (*c*) those soluble both in alcohol and alkalis (Hoppe-Seyler, *H.* 13, 66).

HYÆNIC ACID $C_{25}H_{50}O_2$. Mol. w. 382. [78°]. The glyceride of this acid is said to occur together with palmitin and oleïn in the anal glandular pouches of the striped hyæna (Carius, *A.* 129, 168). According to Schulze a. Ulrich (*B.* 7, 570), it also occurs in the product of the saponification of the grease of sheep's wool. Granules composed of minute curved needles (from alcohol); resembles cerotic acid; sl. sol. cold alcohol, v. sl. sol. ether. Ppd. by alcoholic lead acetate sooner than palmitic acid.—CaA'_2: [90°]; white crystalline powder.—PbA'_2: white pp.

HYALINS *v.* Proteïds, *Appendix C.*

HYALOGENS *v.* Proteïds, *Appendix C.*

HYDANTOÏN $C_3H_4N_2O_2$ *i.e.*


$CO\left\langle\begin{matrix}NH.CH_2\\NH.CO\end{matrix}\right\rangle$. *Glycollyl-urea. Di-oxy-meta-pyrazole.* Mol. w. 100. [215°].

Formation.—1. Together with urea, by the action of conc. HIAq at 100° on allantoïn (Baeyer, *A.* 117, 179; 130, 158).—2. Together with a small quantity of allanturic acid, by the action of HI on alloxanic acid (B.).—3. By the action of an excess of alcoholic NH_3 on bromo-acetyl bromide (Baeyer, *B.* 8, 612).

Properties.—Colourless needles, m. sol. cold, v. sol. hot, water. Neutral to litmus. Has a somewhat sweet taste. Not attacked by boiling dilute acids, but converted by boiling baryta-water into hydantoic acid. May be oxidised to allanturic acid. Ammoniacal $AgNO_3$ gives a pp. of $AgC_3H_3N_2O_2$ aq.

Hydantoic acid $C_3H_6N_2O_3$ *i.e.* $NH_2.CO.NH.CH_2.CO_2H$. *Uramido-acetic acid. Glycolluric acid.*

Formation.—1. By boiling hydantoïn with baryta-water or potash (Baeyer, *A.* 130, 160).—2. Together with urea, by boiling glycoluril $C_4H_6N_4O_2$ with baryta-water (Rheineck, *A.* 134, 222).—3. By heating glycocoll with a slight excess of urea at 120° (Heintz, *A.* 133, 70; Griess, *B.* 2, 106).—4. By the action of cyanic acid on glycocoll; *i.e.* by heating glycocoll sulphate with potassium cyanate, ppg. potassium sulphate by alcohol, and allowing the liquid to evaporate spontaneously (Wislicenus, *A.* 165, 103).—5. By heating glycocoll with urea; or, better, by boiling these substances with baryta-water (Baumann a. Hoppe-Seyler, *B.* 7, 34).

Properties. — Monoclinic prisms; $a{:}b{:}c = \cdot662{:}1{:}\cdot535$; $\beta = 81°\ 0'$. M. sol. cold water and alcohol, v. sol. hot water and alcohol, nearly insol. ether.

Reactions.—1. Decomposed by heating with conc. HIAq at 165° to CO_2, NH_3, and glycocoll (Menschutkin, *A.* 153, 105).—2. Pure HNO_3 forms a nitro- derivative, no gas being evolved (Franchimont, *R. T. C.* 6, 217).

Salts.—These are all, except the Ag salt, v. sol. water.—KA': minute, six-sided tables and rhombohedra.—NaA'aq: extremely soluble silky needles.—NH_4A'aq: large crystals, becoming opaque from loss of NH_3.—BaA'_2 2aq (at 100°): amorphous, insol. alcohol.—PbA'_2 3aq: nodules. —AgA': pearly scales.

References.—Ethyl, Methyl-, Phenyl-, Phenyl-ethyl-, Styryl-, Nitro- and Thio-hydantoïn and Hydantoïc acid.

HYDRACIDS. As explained in the article Acids (vol. i. p. 47) those compounds of hydrogen which, in presence of water, react with metallic oxides, hydroxides, and carbonates, and exchange the whole of their hydrogen, or a portion of it, for metal, are called *acids*. The element common to all acids is hydrogen; but it is only when hydrogen is intimately associated in a compound with one or more strongly negative elements that the compound has the properties of an acid. The greater number of acids contain oxygen, but the presence of this element is not necessarily accompanied by acidic function, nor is its absence proof that we have to deal with a non-acidic compound. Solutions of the following compounds contain acids: HF, HCl, HBr, HI, HCN, HSCN, HSeCN, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, $H_4Co(CN)_6$, $H_3Co(CN)_6$, $HAu(CN)_4$, $H_3Ir(CN)_6$, $H_4Mn(CN)_6$, $H_4Os(CN)_6$, $H_2Pt(CN)_4$, $H_4Ru(CN)_6$, $H_2Pt(SCN)_4$, $H_2Pt(SCN)_6$, $HAuCl_4$, H_2HgI_4, HBF_4, H_2S, H_2SnS_3, H_2CS_3. These acids, and a few more, do not contain oxygen. Acids which are not compounds of oxygen are sometimes classed together as *hydracids*. The name is more particularly applied when it is desired to distinguish between two classes of compounds of the same elements, or group of elements, both of which classes are acids, but only one class is formed of oxygen compounds; thus we speak of the oxy-acids and the hydracids of the halogen elements. The terms hydracid is then only a convenient word when we wish to emphasise the fact that an acid under consideration is not an oxygen compound. All acids are hydracids, as all are compounds of hydrogen. M. M. P. M.

HYDRACRYLIC ACID $C_3H_6O_3$ *i.e.* $CH_2(OH).CH_2.CO_2H$. *β-Oxy-propionic acid. Ethylene-lactic acid.* (β)-*Lactic acid.*

Formation.—1. By digesting β-iodo-propionic acid with excess of moist Ag_2O, decomposing the resulting silver salt by H_2S, filtering, neutralising with Na_2CO_3, and evaporating (Beilstein, *A.* 122, 366; Sokoloff, *A.* 150, 167). Acrylic, dihydracrylic $C_6H_{10}O_5$, and the isomeric para-adipo-malic acids (*v.* vol. i. p. 63) are formed, but are left undissolved when sodium hydracrylate is dissolved in 95 p.c. alcohol (Wislicenus, *B.* 4, 522; *A.* 166, 6).—2. Together with acrylic acid by boiling β-iodo-propionic acid with milk of lime. The impure acid may be converted into the zinc-calcium salt, which can be purified by recrystallisation, and then decomposed by H_2S and the calculated quantity of oxalic acid (Heintz, *A.* 157, 291).—3. By boiling β-iodo-propionic acid with a large excess (25 pts.) of water (Thomson, *A.* 200, 81).—4. By boiling sodium acrylate with aqueous NaOH (Linnemann, *B.* 8, 1095; Erlenmeyer, *A.* 191, 281).—5. From glycol chlorhydrin and KCN, followed by saponification of the product (Wislicenus, *A.* 128, 4; Erlenmeyer, *A.* 191, 268).—6. From ethylene oxide and HCN and saponification of product (Erlenmeyer, *A.* 191, 269).

Properties.—Strongly acid syrup, resolved by heat into water and acrylic acid. Unlike lactic acid it does not yield iodoform when heated with iodine and potash (Lieben's reaction).

Reactions.—1. Boiling with H_2SO_4 (1 pt.) diluted with water (1 pt.) converts it into water and acrylic acid.—2. *Chromic acid* oxidises it to CO_2 and oxalic acid. *Nitric acid* acts in like manner.—3. Ag_2O oxidises it to oxalic and glycollic acids.—4. *Potash-fusion* gives formic and acetic acids.—5. HI gives β-iodo-propionic acid.

Salts.—NaA': [143°]; flat deliquescent prisms, sl. sol. boiling alcohol. At 250° it gives acrylic and para-adipo-malic acids (Wislicenus, *A.* 174, 286).—CaA'_2 2aq: [140°-145°]; prisms, very easily soluble in cold water, insol. alcohol. Forms with calcium acrylate a compound $Ca(C_3H_5O_3)(C_3H_3O_2)$ aq.—ZnA'_2 4aq: [60°], triclinic crystals. S. 112 at 16·5° (Wislicenus).—$CaZnA'_4$: crystalline pp. formed on mixing the concentrated solutions of the zinc and calcium salts. S. 9 at 15°. Scarcely more soluble in hot than in cold water. Insol. boiling alcohol and ether.—AgA': delicate prisms and needles, v. sol. cold water, insol. alcohol.

Nitrile $CH_2(OH).CH_2.CN$. *Glycol cyanhydrin.* (221°) at 724 mm. S.G. º 1·059. S. (ether) 2·3 at 15°. From ethylene oxide and dry HCy at 55° (Erlenmeyer, *A.* 191, 273). Liquid, miscible with alcohol and water.

Dihydracrylic acid $C_6H_{10}O_5$ *i.e.* $O(CH_2.CH_2.CO_2H)_2$. One of the products obtained by boiling β-iodo-propionic acid with Ag_2O and water (Wislicenus, *A.* 166, 39).—Na_2A'': silky crystalline mass; insol. 95 p.c. alcohol, sol. hot 90 p.c. alcohol. Converted by HI into β-iodopropionic acid. Its aqueous solution gives with lead nitrate a flocculent pp., sol. excess.

HYDRAMIDES. Compounds of the form N_2R_3, obtained by the action of ammonia on certain aldehydes, chiefly aromatic, *e.g.* furfuraldehyde and benzoic aldehyde. They are crystalline solids, insol. water, sol. alcohol. They are not volatile, and are decomposed by acids into NH_3 and the parent aldehyde.

HYDRASTINE $C_{21}H_{21}NO_6$. [132°] (F. a. W.). $[\alpha]_D = -67·8°$ (2·5 g. dissolved in 100 c.c. chloroform); $= +127°$ in HClAq. An alkaloid discovered by Perrins (*Ph.* [2] 3, 546) in the root of *Hydrastis canadensis*, or Golden Seal, in which it exists to the amount of 1½ p.c., together with berberine, and possibly a third alkaloid, canadine (Van der Espt, *Ph.* [3] 3, 604; Hale, *Ph.* [3] 4, 105; Burt, *Ph.* [3] 6, 467; Lloyd, *Ph.* [3] 10, 125; Freund a. Will, *B.* 19, 2797; 20, 88, 2400; Schmidt a. Wilhelm, *Ar. Ph.* [3] 26, 329; Eijkman, *R. T. C.* 5, 290; Power, *Ph.* [3] 15, 297; 16, 1092; Lyons, *Ph.* [3] 16, 880; Mahla, *Am. S.* [2] 36, 57). Occurs also in *Stylophorum diphyllum* (Eijkman).

Hydrastine is best obtained by extracting the root of *Hydrastis* with ether, and recrystallising the extract from alcohol (F. a. W.). Trimetric crystals, $a:b:c = ·846:1:·376$. Almost insol. water, sl. sol. cold alcohol, v. sol. boiling alcohol and chloroform. It has a bitter taste, producing a feeling of numbness in the mouth. It does not appear to be poisonous.

Reactions.—1. Boiling dilute *nitric acid* forms opianic acid and hydrastinine. MnO_2 and H_2SO_4 give the same products.—2. $KMnO_4$, in presence of HCl, also forms opianic acid.—3. $KMnO_4$ in alkaline solution forms hemipic acid and pyridine carboxylic (nicotinic) acid.—B'HCl.—$B'_2H_2PtCl_6$.—$B'(HAuCl_4)_2$.—$B'H_2SO_4$.—**Picrate.** $B'C_6H_2(NO_2)_3OH$ 4aq: yellow needles (from alcohol).

Methylo-iodide B'MeI. [208°]. Needles (from water or alcohol). With moist Ag_2O it gives crystals [237°].

Ethylo-iodide B'EtI. [206°] (S. a. W.); [124°] (Eijkman); [183°] (Power). Gives rise to

$(B'EtCl)_2PtCl_4$ [207°], $B'EtClAuCl_3$ [c. 110°], and B'EtOH, which may be crystallised from hot water.

Hydrastinine $C_{11}H_{11}NO_2$aq or $C_{11}H_{13}NO_3$ *i.e.* $CHO.C_7H_4O_2.CH_2.CH_2.NHMe$ (?) (W. Roser, *A.* 240, 156). [117°]. Obtained, together with opianic acid, when hydrastine is treated with oxidising agents (F. a. W.). White needles (from ligroïn), v. e. sol. alcohol and ether, m. sol. hot water. Crystallises from all solvents with aq. Somewhat decomposed when recrystallised from benzene or EtOAc. Its aqueous solution is strongly alkaline and intensely bitter. Ppd. from its solution in acids by KOH but not by NH_3 or Na_2CO_3. Reduced by Zn and HCl to hydrastinine dihydride. Boiling aqueous KOH forms hydrastinine dihydride and oxyhydrastinine. MeI forms a volatile base and an indifferent oil which yields an oxim [129°].

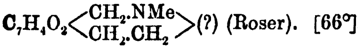
Salts.—B'HCl: [c. 212°]; needles, v. sol. alcohol and water. Its aqueous solution shows a feeble fluorescence, and is optically inactive.—$B'H_2SO_4$: sol. alcohol.—$B'H_2Cr_2O_7$: slender golden needles, sol. water. Decomposes at 175°.—$B'H_2PtCl_6$.

Methylo-iodide B'MeI: slender yellow needles, sol. water and alcohol.

Oxim $C_{10}H_{12}NO_2CH{:}NOH$. [146°]. Formed by boiling the base (1 g.) with hydroxylamine hydrochloride (½ g.) and alcohol (20 c.c.) for a few minutes, and then adding NH_3Aq (Freund, *B.* 22, 457). Needles (from alcohol).—$B'_2H_2PtCl_6$: crystalline pp.

Hydrastic acid $C_8H_7NO_4$. [232°]. Formed by boiling hydrastine with dilute HNO_3 until KOH no longer ppts. the product. Crystalline, sol. alcohol and water. Resembles apophyllic acid.—AgA': needles.

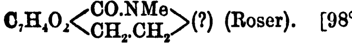
Hydro-hydrastinine $C_{11}H_{13}NO_2$ *i.e.*


$C_7H_4O_2{<}\begin{smallmatrix}CH_2.NMe\\CH_2.CH_2\end{smallmatrix}{>}$ (?) (Roser). [66°]. Formed by reducing hydrastine with zinc and HCl. White crystals, v. e. sol. alcohol, ether, benzene, and CS_2. Re-oxidised by chromic acid mixture to hydrastine.

Salts.—B'HCl: [274°]; crystals, sl. sol. water.—$B'_2H_2PtCl_6$: [216°]; yellow scales.—B'HBr: [272°]; tufts of small white needles sl. sol. water.—B'HI: [232°].—$B'_2H_2Cr_2O_7$: red scales; explodes at 150°.

Ethylo-iodide B'EtI: [207°]; needles.

Oxy-hydrastinine $C_{11}H_{11}NO_3$ *i.e.*


$C_7H_4O_2{<}\begin{smallmatrix}CO.NMe\\CH_2.CH_2\end{smallmatrix}{>}$ (?) (Roser). [98°]. (above 350°). Formed, together with the preceding, by the action of aqueous KOH upon hydrastinine. Prepared by rubbing up hydrastinine with water and potash-ley, shaking, and adding a cold saturated solution of $K_2Mn_2O_8$ till decolourisation proceeds slowly; then filtering, extracting the residue with ether, neutralising, and evaporating the filtrate (Martin Freund, *B.* 22, 457). Needles, v. e. sol. alcohol, chloroform, and benzene. Feeble base. By dissolving in dilute HNO_3 it is converted into a crystalline nitro- derivative $C_{11}H_{10}(NO_2)NO_3$ [271°], insol. HCl, ammonia, or Na_2CO_3Aq, sol. warm NaOHAq.—B'HCl: [138°]; crystalline. Decomposed by water and by alcohol.—$B'_2H_2PtCl_6$: [160°]; yellow needles.—$B'_2H_2AuCl_8$: [100°]; reddish-brown mass.

Dibromo-hydrastinine $C_{11}H_9Br_2NO_3$. [c. 280°]. Formed by exposing a solution of the hydrobromide of hydro-hydrastinine to bromine vapour (Freund). Broad white needles (from hot water). In solutions of its salts NH_3, caustic soda, and Na_2CO_3 give a pp. which crystallises from alcohol in slender thread-like needles [125°].

Di-iodo-hydrastinine hydriodide (so-called) $C_{11}H_{11}I_2NO_2HI$. [134°]. A substance formed by boiling hydrastinine for some minutes with fuming HIAq (Freund). Crystallises from alcohol in splendid brown needles.

Constitution.—Narcotine $C_{19}H_{14}(OMe)_3NO_4$ is perhaps methoxy-hydrastine, hydrastine being $C_{19}H_{15}(OMe)_2NO_4$. Hydrastinine would then contain no methoxyl, while cotarnine would be methoxyl-hydrastinine (Schmidt a. Wilhelm, *Ar. Ph.* [3] 26, 329).

HYDRATES. Compounds of water with other compounds or with elements. If Cl is passed into ice-cold water a yellowish white solid is produced, which when dried between paper at 0° forms a white mass of crystals having the composition $Cl.5H_2O$; heated to 35° in a closed tube the crystals separate into Cl and water, and on cooling to 15° the compound $Cl.5H_2O$ is again produced. The compound $Cl.5H_2O$ is a hydrate of Cl, *i.e.* it is a compound of Cl with water. When BaO is brought into contact with water combination occurs, and $BaO.H_2O$ is produced; this compound is not changed by the action of heat alone. It is customary to call $BaO.H_2O$ an hydroxide, and to regard it as a compound of Ba, O, and H, rather than a compound of BaO with H_2O. If water is added to CaO (an oxide very similar to BaO), combination occurs, and $CaO.H_2O$ is produced; at a full red heat this compound is resolved into its constituents, CaO and H_2O. The compound formed by the union of CaO and H_2O is sometimes called a hydrate, and its formula is written $CaO.H_2O$; but by some chemists it is called an hydroxide, and the formula assigned to it is CaO_2H_2 or $Ca(OH)_2$. Compounds formed by the union of molecules of H_2O with other molecules or atoms, without a rearrangement of the atoms of the group H_2O, are called hydrates; compounds formed by a reaction of molecules of H_2O with other molecules or atoms, such that the group H_2O is separated into its constituent atoms, which are rearranged in the new molecule, are called hydroxides. But it is often impossible to tell whether a given compound is an hydrate or an hydroxide. The definition given above is a theoretical definition; we have no certain means of telling to which class a specified substance belongs. Another way of stating the theoretical difference between hydrates and hydroxides is to say that hydrates contain water as such, and that hydroxides contain the elements of water. Another form of words sometimes used is to speak of *water of hydration*, or *water of crystallisation*, and to contrast this with *water of constitution*. Cane sugar, for instance, has the composition $C_{12}H_{22}O_{11}$. Did we know nothing about cane sugar except its composition we might write the formula $C_{12}H_{22}O_{11}$ as $C_{12}.11H_2O$; but the properties of cane sugar make it evident that it is not a compound of carbon with water, but a compound of C, H, and O, in which the H and O are in the same ratio as in H_2O. We may say of cane sugar that it is an hydroxide, or that it contains the elements of water, or that it contains water of constitution. Copper sulphate, $CuSO_4$, combines with water to form blue crystals $CuSO_4.5H_2O$; when these crystals are heated to 220° or so, the water is all removed, and white $CuSO_4$ remains; these changes—hydration and dehydration—may be repeated indefinitely. We may say then that the blue crystals of copper sulphate contain water of crystallisation.

The term hydroxide is sometimes used in a narrower sense than explained above; by some chemists it is applied only to compounds whose reactions are best explained by supposing them to contain the group or radicle OH.

The problem suggested by the terms hydrate and hydroxide is not one merely of nomenclature; it is a typical problem of chemistry. The two terms attempt to summarise certain conceptions regarding connexions between the properties and the composition of certain compounds. Here, as in other chemical problems, we must study composition and properties, and we must beware of divorcing the one study from the other.

When Zn reacts with dilute H_2SO_4Aq to form $ZnSO_4$, we know that the $ZnSO_4$ must contain the zinc as such; yet the properties of the Zn are modified by its combination with the radicle SO_4. The $ZnSO_4$ produced is a substance by itself; it has its own properties very different from those of any of its constituents. In a sense it is hardly accurate to say that zinc sulphate contains zinc; zinc sulphate is a new thing in which the properties of Zn, S, and O are merged. Zinc sulphate is as distinctly a definite homogeneous kind of matter as any of the elements which combine to form it. From it we can obtain Zn, S, and O; none of these three kinds of matter have we yet been able to separate into unlike parts. But when water combines with other substances, we are dealing with a body which we are able to separate into unlike parts; and, therefore, we may suppose either that the water combines as a whole with the other substance, or that a rearrangement of the atoms of the reacting bodies occurs, and that in the new compound the relation of the O and H atoms are different from those which hold good in the molecule H_2O.

The problem is similar to that presented by questions about the presence of this or that radicle, or group of atoms, in the molecules of carbon compounds; it also presents analogies with questions regarding molecular and atomic compounds. We cannot, as a rule, isolate the radicles which, we suppose, form groups of closely related atoms in the molecules of carbon compounds; we can, however, isolate the radicles which form groups of closely related atoms in the molecules, or at least in the chemically reacting weights, of double salts (*v.* DOUBLE SALTS, p. 414). We can isolate the radicle, or group of atoms, H_2O; the molecule, or the chemically reacting weight, of a hydrate is supposed to be so constituted that one of its radicles is the group H_2O; whereas this group is supposed to be absent from the molecule of an hydroxide. If a compound is a hydrate we should expect it to reveal its constitution by its properties and reactions: the radicle H_2O will carry with it certain characteristic properties different from those which belong to the radicle OH.

The methods by which attempts are made to differentiate hydrates from hydroxides consist partly in studying the chemical reactions of the compounds, and partly in determining their physical properties and comparing these with those of well-defined compounds belonging some to one class and some to the other.

Compounds formed by the reactions of water with other compounds or elements, and which are separated by heat into water and the other constituent from which they have been produced, are usually, but not in every instance, classed as hydrates. Some compounds are decomposed by heat with production of water and another substance, but are not produced by the direct union of water with the other substance; some of these compounds are classed as hydrates, some are not. Thus the compound CuO_2H_2, which is decomposed by heat to CuO and H_2O, is generally regarded as hydrated copper oxide, $CuO.H_2O$; it is obtained by ppg. a solution of a Cu salt by an alkali, but it is not formed by the direct union of CuO and H_2O. But the compound AsO_4H_3 is not called a hydrate, although it is resolved by heat into As_2O_5 and H_2O ($2H_3AsO_4 = As_2O_5 + 3H_2O$).

The reasons for regarding CuO_2H_2 as a hydrate, and for not placing AsO_4H_3 in this class, are based on the chemical analogies of these compounds. CuO_2H_2 is very similar, in its methods of formation and properties, to compounds which are undoubtedly hydrated compounds. AsO_4H_3 is an acid; the hydrogen of this compound can be replaced by certain metals; now acids as a class exhibit properties which undoubtedly show that they are not compounds of water.

Some compounds formed by the reaction of water with another compound are classed as hydrates, and some are not placed in this class. A compound may be formed by the union of water with another substance, and the compound may be resolved into water and the other substance, either by the action of heat or a dehydrating agent, and yet the compound in question is not necessarily placed among the hydrates. Water, for instance, reacts with N_2O_5 to form nitric acid, and nitric acid loses water, forming N_2O_5, by reacting with P_2O_5; yet nitric acid is not to be classed as a hydrate. Here again the properties and reactions of the compound formed by the reaction of water forbid us to regard it as a hydrate. The arguments against calling nitric acid a hydrate are not drawn solely from the reactions of this compound, but also from the general reactions of acids.

In discussing whether a specified compound is or is not a hydrate, regard must be paid to the chemical analogies of the compound, and to the reactions of compounds with which it is allied. Thus it is the custom to regard the compounds MO_2H_2, where M = Ca, Sr, or Ba, as hydroxides rather than hydrates. One of the reasons for this is based on the undoubted similarities between these compounds and the compounds MOH, where M = an alkali metal. The latter compounds are certainly hydroxides; among the reasons for this statement is the analogy in chemical reactions—*e.g.* reactions with acids and with PCl_5—between these compounds and the monohydric alcohols $C_nH_{2n+1}OH$. These alcohols cannot be called hydrates; they are not formed by the union of water with the hydrocarbons C_nH_{2n+2}; they are produced by reactions between iodo- derivatives of the paraffins and KOH; they react with PCl_5 to form chloroparaffins $C_nH_{2n+1}Cl$. The compound formed by the reaction of Na_2O with H_2O may be formulated, so far as composition goes, as $Na_2O.H_2O$ or as NaOH. If the molecular weight were found to be 40, the formula NaOH would necessarily be adopted. In the absence of this evidence, we must have recourse to a study of the reactions of the compound. The weight of caustic soda which reacts with one molecular weight of hydrochloric acid (HCl) is expressed by the number 40; the same number expresses the weight of this compound which reacts with one atom of sodium; hence we adopt 40 as the reacting weight of caustic soda; and hence we write the formula NaOH and not $Na_2O.H_2O$ (or NaO_2H_2). One reason for writing the formula of caustic baryta BaO_2H_2 and not $BaO.H_2O$ is found in the close analogies between this compound and caustic soda. Caustic baryta combines with water to form a compound $BaO_2H_2.8H_2O$; this compound is said to be a hydrated hydroxide; a hydrate, because $8H_2O$ can be removed by heat; an hydroxide, for the reasons already given. A great mass of data regarding the dehydration of metallic hydroxides and hydrated oxides by heat is given in a paper by Carnelley a. Walker, *C. J.* 53, 59.

The specific volumes, or molecular volumes, of compounds formed by interaction of water with other compounds throw some light on the distinction between hydrates and hydroxides. The specific, or molecular, volume of a solid compound is defined as $\frac{\text{formula-weight}}{\text{spec. grav.}}$; this quotient may be represented by (V). Clarke (*Am. S.* [3] 8, 428) has determined (V) for a number of compounds formed by interactions of water with other compounds. He finds that for many hydrated chlorides the mean value of

$$\frac{(V)MCl_2.xH_2O - (V)MCl_2}{x}$$

is 13·76; the maximum value being 15 and the minimum 12·5. In the chlorides examined M was Ca, Sr, Ba, Mg, Cu, Fe, and Co; and x varied from 2 to 6. Values for (V) for the following compounds were also obtained: $B_2O_3.3H_2O$, $I_2O_5.H_2O$, $K_2O.H_2O$, $CaO.H_2O$, $SrO.H_2O$, $BaO.H_2O$, $Al_2O_3.H_2O$, $Mn_2O_3.H_2O$, $Fe_2O_3.H_2O$. Values were also obtained for (V) for the oxides B_2O_3, I_2O_5, K_2O, &c. The difference

$$\frac{(V)\text{ oxide }xH_2O - (V)\text{ oxide}}{x}$$

varied from 7·4 to 19·4.

Hence it appears that the specific volume of each H_2O in hydrated chlorides has a mean value of about 13·76, and that in no case does the actual value differ much from this; but that no simple relation can be traced between (V) for an oxide and (V) for the product of the combination of that oxide with water in those cases in which we have reason to believe that a rearrangement of the atoms of the molecule H_2O has taken place.

Perkin (*C. J.* 1886. 777) has used measurements of the magnetic rotatory powers of compounds (Mol. R.) to attempt a distinction between water of constitution and water of hydration. (Mol. R.) of water is taken as unity; if then (Mol. R.) of a compound is x, and if (Mol. R.) of the compound formed by adding water to this compound is increased by about 1 for each H_2O that has entered into combination, we may conclude that the new compound is a hydrate. The following examples are taken from Perkin's paper:—

(Mol. R.) of $H.CO_2H = 1\cdot671$;
(Mol. R.) of $HCO_2H.H_2O = 1\cdot676 + \cdot995$.
(Mol. R.) of $CH_3.CO_2H = 2\cdot525$;
(Mol. R.) of $CH_3.CO_2H.H_2O = 2\cdot525 + 1\cdot029$.
(Mol. R.) of many organic acids *minus* (Mol. R.) of the corresponding anhydride = c. ·74.
(Mol. R.) of $H_2SO_4 = 2\cdot315$;
(Mol. R.) of $H_2SO_4.H_2O = 2\cdot315 + \cdot873$.
(Mol. R.) of $H_2SO_4.H_2O = 3\cdot188$;
(Mol. R.) of $H_2SO_4.2H_2O = 3\cdot188 + \cdot925$.
(Mol. R.) of $CCl_3.CHO = 6\cdot591$;
(Mol. R.) of $CCl_3.CHO.H_2O = 6\cdot591 + \cdot446$.

The compounds formed by the union of formic and acetic acids with water appear to be hydrates. The compound formed by the union of sulphuric acid with water in the ratio $H_2SO_4{:}H_2O$ appears to be an hydroxide (Perkin thinks it may be $SO(OH)_4$), but the combination of more water with the compound thus produced is probably a process of hydration. Chloral hydrate is probably not a hydrate, but rather trichloro-ethylidene glycol $CCl_3.CH(OH)_2$.

Differences can be traced between the various H_2O groups in some hydrated salts. Thus $CuSO_4.5H_2O$ loses $4H_2O$ at about 100°, but the fifth H_2O only at c. 220°; $Na_2CO_3.10H_2O$ at 12·5° loses $5H_2O$, at c. 38° the hydrate $Na_2CO_3.H_2O$ remains, and complete dehydration occurs by heating towards redness. (Regarding the formation of different hydrates of the same salt from solutions *v.* Hammerl, *M.* 3, 419.) Thorpe and Watts (*C. J.* Trans. 1880. 102) have determined the specific volumes of various hydrated and dehydrated sulphates, $MSO_4.xH_2O$, where M = Mg, Zn, Cu, Mn, Fe, Co, and x varied from 1 to 7. Putting (V) S as specific volume of the dry sulphate, they get the following results:—

Mean difference between
(V) S and (V) S. $H_2O = 10\cdot7$
" " " (V) S. $2H_2O = 13\cdot3$
" " " (V) S. $3H_2O = 14\cdot5$
" " " (V) S. $4H_2O = 15\cdot4$
" " " (V) S. $7H_2O = 16\cdot2$.

Hence each H_2O group raises (V) to a different extent.

Sodium phosphate crystallised from solutions at the ordinary temperature has the composition $Na_2HPO_4.12H_2O$; the crystals which separate at 33° are $Na_2HPO_4.7H_2O$; there are also hydrates intermediate between these, and hydrates with less water than $7H_2O$. If one of these hydrates is heated in a closed space water is evolved, and the pressure increases until at a certain pressure the change stops and equilibrium is produced. A study of the equilibrium-pressures discloses a marked difference between the hydrates with 7 and 12 H_2O. Debray (*C. R.* 66, 195) gives the following numbers :—

Equilibrium pressures.

Temp.	Salt with more than 7 and up to $12H^2O$	Salt with 7 or less than $7H^2O$
12·3°	7·4 mm.	4·8 mm.
16·3°	8·9 „	6·9 „
20·7°	14·1 „	9·4 „
24·9°	18·2 „	12·9 „
31·5°	30·2 „	21·3 „

It is evident that the distinction between hydrates and hydroxides is not one which can be rigidly drawn. One class of compounds shades off into the other. There is no means by using which we can refer any specified compound to this class or to that. Many reactions must be studied for each compound, and the classification finally adopted is generally only provisional.

M. M. P. M.

HYDRAZIDES *v.* HYDRAZONES. The phenyl-hydrazides of aldehydes and of ketones are described under the aldehydes and ketones from which they are prepared. Hydrazides are formed by elimination of water between an oxygenated body and a hydrazine. Elimination of water between an oxygenated body and an amine forms an amide or imide.

HYDRAZIDO-BENZENE SULPHONIC ACID *v.* PHENYL-HYDRAZINE SULPHONIC ACID.

HYDRAZIDO-BENZOIC ACID *v.* PHENYL-HYDRAZINE CARBOXYLIC ACID.

***o*-HYDRAZIDO-CINNAMIC ACID** $NH_2.NH.C_6H_4.CH:CH.CO_2H$. [171°]. From diazo-cinnamic acid by converting it first by Na_2SO_3 into $SO_3Na.N_2.C_6H_4.CH:CH.CO_2H$, then reducing by hydrochloric acid and zinc-dust to $SO_3Na.NH.NH.C_6H_4.CH:CH.CO_2H$, and finally decomposing this by HCl gas (Fischer a. Kuzel, *A.* 221, 276; *A.* 227, 303). Yellowish crystals. Nearly insol. water, alcohol, ether, benzene, or light petroleum. Sol. alkalis and acids. Its acetic acid solution bleaches litmus and indigo (unlike the simpler hydrazines), reduces alkaline copper solution, and ammoniacal silver solution. When melted it forms indazole (*q. v.*).

Salt.—HA'HCl: [146°]; yellowish crystalline powder, soluble in alkalis, reduces Fehling's solution in the cold. Heat changes it to indazole (*q. v.*), not into its anhydride.

Anhydride *v.* AMIDO-CARBOSTYRIL.

***o*-HYDRAZIDO-PHENOL.**

Methyl ether $C_6H_4(OMe)NH.NH_2$. [43°]. *Methoxy-phenyl-hydrazine.* From $C_6H_4(OMe).NH.NH.SO_3H$ and conc. HCl (Reisenegger, *A.* 221, 319). Slender white needles, which turn brown in air. Insol. water, v. sol. alcohol, ether, and benzene. Reduces Fehling's solution, HgO, and ammoniacal $AgNO_3$. With cyanic ether it forms a urea (semicarbazide) $MeO.C_6H_4.N_2H_2.CO.NHEt$ [110°] needles.

Salts.—B'HCl.—$B'_2H_2C_2O_4$.—$B'C_6H_2(NO_2)_3OH$.

Acetyl derivative $C_6H_4(OMe)N_2H_2Ac$: [125°]; needles.

***o*-HYDRAZIDO-PHENOL-*v*-SULPHONIC ACID.**

Salt. — $HO.C_6H_4.NH.NH.SO_3K$. From $HO.C_6H_4.N_2.SO_3K$, zinc-dust and glacial HOAc (Reisenegger, *A.* 221, 315). White plates. Quickly turns red when moist. V. sol. water, the solution being very unstable. Reduces Fehling's solution.

Methyl derivative $MeO.C_6H_4NH.NH.SO_3H$.

Salt.—NaA'aq. From $C_6H_4(OMe)NH_2$ by diazotisation and treatment with Na_2SO_3 (R.). Plates. Reduces cold Fehling's solution. Warmed with conc. HCl it forms *o*-hydrazido-phenol methyl ether (*q. v.*).

***p*-Hydrazido-phenol *v*-sulphonic acid.**

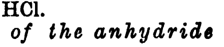
Salt. — $HO.C_6H_4.NH.NH.SO_3K$. Prepared in a similar way from the *p*- compound (R.). White scales, more stable than the *o*- compound. Reduces cold Fehling's solution.

***o*-HYDRAZIDO-β-PHENYL-PROPIONIC ACID.**

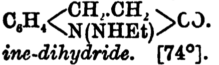
Sodium salt.—$NH_2.NH.C_6H_4.CH_2.CH_2.CO_2Na$ (E. Fischer a. Kuzel, *A.* 221, 282). This salt may be got by reducing $C_6H_4(NH.NH.SO_3Na).CH:CH.CO_2H$ by sodium amalgam in alkaline solution. Precipitated by adding NaCl and acetic acid. Small crystals, v. sol. water. HCl liberates the acid which at once changes into its anhydride, amido-hydrocarbostyril (*q. v.*) [143°].

Ethyl-hydrazido-phenyl-propionic acid $C_6H_4(NEt.NH_2).CH_2.CH_2CO_2H$. *Ethyl-hydrazine-hydrocinnamic acid.* Formed by reduction of the nitrosamine of ethyl-*o*-amido-phenyl-propionic acid by zinc-dust and glacial acetic acid (E. Fischer a. Kuzel, *A* 221, 294; *B.* 16, 1451). Reduces Fehling's solution on warming. Evaporated with glacial acetic acid it changes to ethyl-hydro-carbazo-styril.

Salts.—BaA'_2: crystals.—HA'HCl. [146°]. At 160° it gives off HCl and H_2O becoming ethyl-hydro-carbazostyril.

Anhydride  $C_6H_4{<}\begin{matrix}CH_2.CH_2\\NEt.NH\end{matrix}{>}CO$. *Ethyl-hydro-carbazo-styril.* [165·5°]. Long white needles, sl. sol. water, v. sol. alcohol and ether. Insol. alkalis, may be distilled unchanged. Warmed with HCl it changes back to the ethyl-hydrazido-phenyl-propionic acid, differing in this respect from hydrocarbostyril which is not changed by hot HCl.

Isomeride of the anhydride

 $C_6H_4{<}\begin{matrix}CH_2.CH_2\\N(NHEt)\end{matrix}{>}CO$. *Oxy-ethyl-amido-quinoline-dihydride.* [74°]. Formed by heating the anhydride of *o*-hydrazido-cinnamic acid with alcohol and EtI at 100° (F. a. K.). Crystals, v. sol. alcohol. sl. sol. water. Gives a nitrosamine.

HYDRAZIDO-TOLUENE SULPHONIC ACID *v.* TOLYL-HYDRAZINE SULPHONIC ACID.

HYDRAZIMIDO-COMPOUNDS *v.* *o*-AMIDO-AZO- COMPOUNDS, vol. i. p. 370.

HYDRAZINE N_2H_4 *i.e.* $NH_2.NH_2$. *Di-amidogen.* Formed by treating diazo-acetic ether with hot conc. KOHAq, decomposing the resulting crystalline potassium salt by HCl, and digesting the yellow crystalline acid so liberated with very dilute sulphuric acid. No gas is evolved, but the solution becomes colourless, and hydrazine sulphate separates on cooling (Curtius, *B.* 20, 1632). Hydrazine sulphate is best obtained by warming tri-azo-acetic acid (250 g. in 2 litres of water) with H_2SO_4 (300 g.) until effervescence ceases. Further quantities may be obtained from the mother-liquor after hydrazine sulphate has crystallised out, by shaking with benzoic aldehyde, and decomposing the resulting crystalline compound with dilute sulphuric acid (Curtius a. Jay, *J. pr.* [2] 39, 27). Hydrazine is only known in its salts and in the form of a hydrate $N_2H_4H_2O$ which is got by heating the hydrochloride in a silver tube with quick lime. This hydrate is a fuming liquid (119°), with very slight odour. It corrodes glass, attacks cork and india-rubber, and has an alkaline and burning taste. Hydrazine reduces Fehling's solution and ammoniacal $AgNO_3$ in the cold. With $CuSO_4$ it gives a thick red pp. of Cu_2O; with $HgCl_2$ a white pp. of calomel; with alum a pp. of alumina. With aromatic aldehydes and ketones it gives sparingly soluble crystalline compounds. Nitrites decompose its salts with evolution of gas.

Salts.—$N_2H_4H_2SO_4$: tables; sl. sol. cold, v. sol. hot, water; insol. alcohol. Not decomposed by heating to 250°; but at a higher temperature it decomposes with explosive evolution of gas, liberating sulphur.—$N_2H_4H_2Cl_2$. [198°]. From the preceding and $BaCl_2$. Large regular crystals; v. sol. cold water, m. sol. alcohol. $PtCl_4$ decomposes it with evolution of gas.—B′HCl: [89°]; long white needles (from hot alcohol). Decomposed at 240° into NH_4Cl, water, and nitrogen, v. sol. water.—Formate $B''(H_2CO_2)_2$: [128°]; got by heating triazo-acetic acid with water. Rectangular tables.

Di-benzylidene hydrazine $N_2(CHPh)_2$. [93°]. From hydrazine sulphate and benzoic aldehyde. Long lustrous yellow prisms; insol. water, sol. hot alcohol. Decomposed by heat into nitrogen and PhCH:CHPh, a by-product being $N_2(CHPh)_4$. [78°]. The molecular weight of di-benzylidene-hydrazine has been confirmed by Raoult's method.

Di-benzyl hydrazine $N_2H_2(CH_2Ph)_2$. Formed by reducing the preceding with sodium-amalgam. Its hydrochloride B′HCl [140°] crystallises from alcohol in small lustrous tables, v. sol. water.

Di-oxy-di-benzylidene hydrazine $N_2(CH.C_6H_4.OH)_2$. [205°]. From salicylic aldehyde and salts of hydrazine. Tables, insol. water and cold alcohol.

Di-nitro-di-benzylidene hydrazine $N_2(CH.C_6H_4.NO_2)_2$. [181°]. From *o*-nitro-benzoic aldehyde and salts of hydrazine. Groups of bright yellow needles.

Di-cinnamylidene-hydrazine $N_2(CH.CH:CHPh)_2$. [162°]. From cinnamic aldehyde and hydrazine salts. Yellow tables.

HYDRAZINES. The name 'hydrazine' was applied by Emil Fischer to the then hypothetical *diamidogen* $H_2N.NH_2$, which he regarded as the parent substance of the *hydrazines*, a large and important class of bases discovered by him, derived from diamidogen by the replacement of either one or two atoms of hydrogen by monad hydrocarbon radicles. The name was intended to indicate the connection of these bases with the azo- and diazo- compounds, and in particular with hydrazobenzene $C_6H_5.NH.NH.C_6H_5$ (symmetrical diphenylhydrazine), the oldest known member of the class of the hydrazines, whilst at the same time the termination 'azine' was formed on the analogy of 'amine,' in order that a parallel nomenclature might be employed in the case of corresponding derivatives of the hydrazines and amines; thus the *hydrazonium* compounds would correspond with the *ammonium* compounds (*A.* 190, 70).

Hydrazine itself has recently been prepared by Curtius, and the analogy between its reactions and those of the compounds discovered by Fischer fully justifies the foregoing classification.

The hydrazines are divided into primary and secondary, according as one or two hydrogen atoms in the original diamidogen molecule have been replaced by hydrocarbon radicles. If the two radicles are attached to different nitrogen atoms the resulting secondary hydrazine is termed *symmetrical*; if to the same nitrogen atom it is *unsymmetrical.* The unsymmetrical secondary hydrazines behave like tertiary amines; they unite with the alkyl halogenides to form *hydrazonium compounds*:

$$NR'_2.NH_2 + R'I = N^{v}R'_3I.NH_2.$$

Preparation.—Hydrazine $NH_2.NH_2$ is formed, together with oxalic acid, when tri-azo-acetic acid is warmed with water or with mineral acids:

$$C_3H_3N_6(COOH)_3 + 6H_2O = 3C_2O_4H_2 + 3N_2H_4.$$

It is as yet known only in the form of its salts and of its hydrate N_2H_4,H_2O (Curtius a. Jay, *J. pr.* [2] 39, 27).

The derivatives containing alkyl and other radicles are obtained by reactions which have no analogy with the foregoing.

Primary hydrazines.—1. The primary hydrazines, of which phenyl-hydrazine $NHPh.NH_2$ may be taken as a type, are most simply obtained by reducing diazo-salts with stannous chloride:

$$Ph.N{:}NCl + 2SnCl_2 + 4HCl$$
$$= Ph.NH.NH_2,HCl + 2SnCl_4$$

(V. Meyer a. Lecco, *B.* 16. 2976).—2. The method originally employed by E. Fischer (*A.* 190, 71), in which sodium sulphite is used as a reducing agent, is more complicated. It gives in some cases a better yield, although occasionally the reverse is the case (*B.* 17, 572). In the first stage of the reaction the diazo-salt is converted by the sodium sulphite into a diazo-sulphonate:

$$Ph.N_2Cl + Na_2SO_3 = Ph.N_2.SO_3Na + NaCl.$$

Hydrochloric acid is then added, which decomposes another molecule of sodium sulphite, and the liberated sulphurous acid or acid sulphite reduces the reddish-yellow sodium diazo-sulphonate to the colourless sodium phenylhydrazine-sulphonate:

$$Ph.N{:}N.SO_3Na + NaHSO_3 + H_2O$$
$$= Ph.NH.NH.SO_3Na + NaHSO_4.$$

Zinc-dust and acetic acid are added to complete the reduction, and the sodium hydrazine-sulphonate is then hydrolysed by heating it with concentrated hydrochloric acid, when it yields phenylhydrazine hydrochloride:

$$Ph.NH.NH.SO_3Na + HCl + H_2O$$
$$= Ph.NH.NH_2,HCl + NaHSO_4,$$

from which the base can be liberated by caustic alkali (E. Fischer, *A.* 190, 78).—3. When a diazo-amido-compound is treated in alcoholic solution with zinc-dust and acetic acid the diazo-group is reduced and the corresponding hydrazine is formed together with an amine:

$$\underset{\text{Diazo-amido-benzene.}}{Ph.N_2.NHPh} + 2H_2 = Ph.NH.NH_2 + Ph.NH_2.$$

$$\underset{\text{Diazobenzene-diethylamine.}}{Ph.N_2.NEt_2} + 2H_2 = Ph.NH.NH_2 + NHEt_2.$$

This method is not of practical importance (E.

Fischer, *A.* 190, 77).—4. The primary hydrazines containing alkyl radicles cannot be obtained by the foregoing reactions, as the diazo- derivatives of the alkyls are unknown. They may, however, be prepared from the nitroso-alkyl-ureas. Thus when nitroso-di-ethyl-urea is reduced with zinc-dust and acetic acid the nitroso- group is converted into an amido- group:

$$\mathrm{CO}<^{\mathrm{NHEt}}_{\mathrm{N(NO)Et}} + 2H_2 = \mathrm{CO}<^{\mathrm{NHEt}}_{\mathrm{N(NH_2)Et}} + H_2O.$$

This amido- compound is then hydrolysed by heating with fuming hydrochloric acid, when it yields ethylhydrazine and ethylamine:

$$\mathrm{CO}<^{\mathrm{NHEt}}_{\mathrm{N(NH_2)Et}} + H_2O$$

$= \mathrm{Et.NH.NH_2} + \mathrm{NH_2Et} + CO_2$ (E. Fischer, *A.* 199, 287).

Secondary hydrazines.—1. The unsymmetrical secondary hydrazines, both in the fatty and in the benzene series, may be obtained by the reduction of the nitrosamines with acetic acid and zinc-dust:

$$\mathrm{NPhMe.NO} + 2H_2 = \mathrm{NPhMe.NH_2} + H_2O$$

(E. Fischer, *A.* 190, 146).—2. The unsymmetrical secondary hydrazines are formed, along with the isomeric symmetrical compounds, by the action of the alkyl halogenides on the primary hydrazines; thus phenylhydrazine yields with ethyl bromide the compounds $\mathrm{NPhEt.NH_2}$ and NPhH.NEtH (E. Fischer a. Ehrhard, *A.* 199, 325). By employing in this reaction sodium-phenylhydrazine $\mathrm{NPhNa.NH_2}$, instead of free phenylhydrazine, only the unsymmetrical compound is formed:

$$\mathrm{NPhNa.NH_2} + \mathrm{EtBr} = \mathrm{NPhEt.NH_2} + \mathrm{NaBr}$$

(Michaelis, *B.* 19, 2450; Philips, *B.* 20, 2485). The unsymmetrical secondary hydrazines formed by alkylation are identical with those obtained by the reduction of the corresponding nitrosamines.

Properties.—The fatty hydrazines are liquids boiling without decomposition; those of the benzene series are either solids of low melting-point or oily liquids, and boil with partial decomposition. Hydrazine itself and some of the fatty hydrazines are diacid bases; others are monacid; the hydrazines of the benzene series are all monacid bases.

Reactions.—1. The hydrazines are very stable towards reducing agents, but are readily attacked by *oxidising agents.* Thus the primary hydrazines reduce *Fehling's solution* in the cold, the secondary on warming. By shaking with *mercuric oxide* the salts of the primary hydrazines are oxidised to diazo- salts; this is most readily shown with potassium phenylhydrazine-sulphonate $\mathrm{Ph.NH.NH.SO_3K}$, which is thus converted into the diazobenzene-sulphonate $\mathrm{Ph.N{:}N.SO_3K}$ (E. Fischer, *A.* 190, 97). The unsymmetrical secondary hydrazines are converted by mercuric oxide into *tetrazones*:

$$2\mathrm{NPhMe.NH_2} + O_2 = \mathrm{NPhMe.N{:}N.NPhMe} + 2H_2O$$

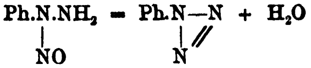
Dimethyl-di-phenyl-tetrazone

(F., *A.* 190, 167), whilst the symmetrical secondary hydrazines are oxidised to azo- compounds:

$$\mathrm{Ph.NH.NHEt} + O = \mathrm{PH.N{:}N.Et} + H_2O$$

Azo-phenyl-ethyl

(E. Fischer a. Ehrhard, *A.* 199, 328).—2. *Nitrous acid* converts the primary hydrazines into nitroso-compounds; thus with phenylhydrazine $\mathrm{Ph.NH.NH_2} + \mathrm{HNO_2} = \mathrm{Ph.N(NO).NH_2} + H_2O$, and when the nitroso- compound thus formed is treated with dilute alkalis it yields diazobenzenimide:



$$\mathrm{Ph.N}\underset{\mathrm{NO}}{|}\mathrm{.NH_2} = \mathrm{Ph.N{-}N} \;(\text{ring with } \mathrm{N}) + H_2O$$

(F., *A.* 190, 89). The unsymmetrical secondary hydrazines, on the other hand, when treated with nitrous acid, are converted with evolution of nitrous oxide into the nitrosamines from which they were obtained: $\mathrm{NPhMe.NH_2} + 2\mathrm{HNO_2} = \mathrm{NPhMe.NO} + N_2O + 2H_2O$ (F., *A.* 190, 159).—3. With the *alkyl halogenides* the primary hydrazines yield a mixture of symmetrical and unsymmetrical secondary hydrazines, whereas sodium-phenylhydrazine gives only the unsymmetrical compound (*v. supra*). The unsymmetrical secondary hydrazines unite directly with an alkyl bromide or iodide to form a *hydrazonium compound*:

$$\mathrm{NEt_2.NH_2} + \mathrm{EtI} = \mathrm{N^vEt_3I.NH_2}$$

Triethylhydrazonium iodide.

That triethylhydrazonium iodide has the foregoing constitution is shown by its behaviour on reduction with zinc-dust and dilute sulphuric acid, when it yields triethylamine, ammonia, and hydriodic acid:

$$\mathrm{N^vEt_3I.NH_2} + H_2 = \mathrm{NEt_3} + \mathrm{NH_3} + \mathrm{HI}$$

(E. Fischer a. Ehrhard, *A.* 199, 316-18).—4. By the action of *acidoyl chlorides* on the primary hydrazines mono- and di- acidoyl derivatives are obtained. Phenylhydrazine yields, by the limited action of *benzoyl chloride*, symmetrical benzoyl-phenylhydrazine Ph.NH.NH.CO.Ph, which by oxidation in chloroform solution with mercuric oxide is converted into *benzoyl-diazobenzene* Ph.N:N.CO.Ph (E. F., *A.* 190, 125). By acting with benzoyl chloride on sodium-phenylhydrazine the unsymmetrical benzoyl-phenylhydrazine $\mathrm{Ph.CO.NPh.NH_2}$ is obtained (Michaelis a. Schmidt, *B.* 20, 1713). Both these monobenzoylphenylhydrazines, when treated with benzoyl chloride, yield the same dibenzoylphenylhydrazine, which has therefore the constitution Ph.CO.NPh.NH.CO.Ph (E. F., *A.* 190, 128; M. a. S., *l.c.*). These acidoyl- derivatives of the hydrazines are the hydrazides of the acids and correspond with the amides, anilides, &c.[1] Thus:

Ph.CO.NHPh	$\mathrm{Ph.CO.N_2H_2Ph}$
Benzanilide (Benzoyl-aniline).	Benzphenylhydrazide (Benzoyl-phenylhydrazine).

A large number of similar derivatives corresponding with the amides and alkyl-amides have been prepared; thus phenylhydrazine hydrochloride reacts with *potassium cyanate* to form *phenylsemicarbazide* $\mathrm{Ph.NH.NH.CO.NH_2}$ (the semi-urea of phenylhydrazine); phenylhydrazine unites with *carbon dioxide* yielding as product *phenylhydrazine phenylcarbazate* $\mathrm{PH.NH.NH.CO.O.N_2H_4Ph}$, and with *carbon disulphide* to form *phenylhydrazine phenylthiocarbazate* $\mathrm{Ph.NH.NH.CS.S.N_2H_4Ph}$ (corresponding respectively with ammonium carbamate and ammonium thio-carbamate), and on heating the latter compound it yields the thiourea *diphenylthiocarbazide* $CS(NH.NHPh)_2$ (E. F., *A.* 190, 113–118). In like manner *azidines* are known, corresponding with the amidines; thus *benzenyldiphenylazidine* $\mathrm{Ph.C}{<}\begin{matrix}\mathrm{N.NHPh}\\ \mathrm{NH.NHPh}\end{matrix}$ (Pinner, *B.* 17, 182).—5. Phenylhydrazine unites directly with *cyanogen* to form dicyano-phenylhydrazine (F.).—6. One of the most important reactions of the hydrazines is that in which they undergo condensation with *compounds containing carbonyl-groups*: thus

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[1] It is, therefore, inaccurate to apply the name 'hydrazides' to the 'hydrazones' (*q. v.*).

$$Ph.CHO + H_2N.NHPh = Ph.CH{:}N.NHPh + H_2O$$

Benzylidene-phenylhydrazine (Benzaldehydrazone).

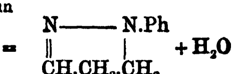
$$Ph_2CO + H_2N.NHPh = Ph_2C{:}N.NHPh + H_2O$$

Benzophenone-phenylhydrazone.

In this way phenylhydrazine may, like hydroxylamine, be employed in testing for the presence of carbonyl-groups in compounds (E. Fischer, *A.* 190, 134; *B.* 17, 572). The compounds thus formed are known as *hydrazones* (*q. v.*). The reaction is occasionally complicated by the presence of other reactive groups, in addition to the carbonyl group, in the molecule of the compound acted upon by phenylhydrazine; thus although compounds containing the *a-ketone-alcohol group* —CH(OH).CO— react in the cold with only one mol. of phenyl hydrazine to form colourless compounds containing the group —CH(OH).C(N.NHPh)—, yet when the compound thus formed is heated with excess of phenylhydrazine the alcohol group undergoes dehydrogenation, reacting at the same time with a second mol. of phenylhydrazine and giving rise to a yellow compound containing the complex —C(N.NHPh).C(N.NHPh)—. Such compounds in which two hydrazine- residues are attached to contiguous carbon atoms are known as *osazones* (*v.* HYDRAZONES) and may also be obtained directly by the action of the hydrazines on the *a*-diketones. They are of great importance in connection with the carbohydrates, which may frequently be recognised by means of their characteristic osazones (E. Fischer, *B.* 17, 579; 20, 821). Again, an unsaturated hydrocarbon group, if contiguous to the carbonyl-group, may also take part in the reaction with phenylhydrazine:

$$CH_2{:}CH.CHO + H_2N.NHPh$$

Acrolein

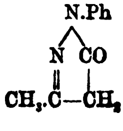


Phenylpyrazoline

(E. Fischer a. Knœvenagel, *A.* 239, 194; *v.* also Knorr a. Blank, *A.* 238, 139). An analogous case is that of ethylic aceto-acetate, which reacts with phenylhydrazine in the cold with elimination of water to form the hydrazone

$$CH_3.C(N.NHPH).CH_2.COOEt;$$

but on heating this compound, it parts with alcohol yielding a phenylpyrazolone of the formula



the carbethoxyl-group also taking part in the reaction (Knorr, *A.* 238, 146). Similar complex condensations have been described with *β*-diketones and with some *γ*-diketones (E. Fischer a. Bülow, *B.* 18, 2135; Paal, *B.* 17, 914; Japp a. Huntly, *C. J.* 1888, 184).

Various other reactions of hydrazines are known, and some of these are doubtless of general application, although they have as yet been applied only in special cases. They will be described under the appropriate hydrazines.

F. R. J.

HYDRAZO-BENZENE *v.* *s*-DI-PHENYL-HYDRAZINE.

HYDRAZO-BENZOIC ACID *v.* DI-PHENYL-HYDRAZINE DI-CARBOXYLIC ACID.

HYDRAZO- COMPOUNDS. Symmetrical di-derivatives of hydrazine, of the formula RNH.NHR′ where R and R′ represent radicles attached by means of carbon to the two atoms of nitrogen (*cf.* HYDRAZINES and *s*-DI-PHENYL-HYDRAZINE). They are described in this dictionary as derivatives of hydrazine.

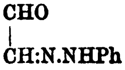
HYDRAZO-HYDROQUINONE *v*-TETRA-OXY-DI-PHENYL-HYDRAZINE.

HYDRAZO-DI-METHYL-HYDROQUINONE *v.* *Tetra-methyl derivative* of TETRA-OXY-DI-PHENYL-HYDRAZINE.

HYDRAZO-NAPHTHALENE *v.* DI-NAPHTHYL-HYDRAZINE.

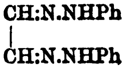
HYDRAZONES. The compounds formed by the condensation of substances containing the carbonyl group with phenylhydrazine were named by many chemists 'phenylhydrazides,' or more shortly, 'hydrazides.' E. Fischer, however (*B.* 21, 984), has pointed out the impropriety of the term. A 'hydrazide' corresponds with an 'amide'; the phenylhydrazido-group is $Ph.N_2H_2$; thus the phenylhydrazide of benzoic acid is $Ph.CO.N_2H_2Ph$. In order to avoid the ambiguity which the above erroneous use of this term introduces, Fischer has proposed to name the compounds in which the dyad group NPhH.N= replaces the oxygen of a carbonyl group 'phenylhydrazones'—the termination *one* serving to suggest their connection with ket*ones* or with carbonyl compounds generally. Further, as in the very great majority of cases it is *phenylhydrazine* which is employed in the preparation of these compounds, the abbreviated form 'hydrazone' may be applied in all such cases, and is to be taken to signify 'phenylhydrazone' unless the contrary is stated. The name 'osazone' is, for reasons to be explained later, applied to any compound containing two dyad groups NPhH.N= attached to two contiguous carbon atoms. Thus in the case of the two compounds obtained from glyoxal and phenylhydrazine we have:

Glyoxalhydrazone



$$\begin{array}{l}CHO\\ |\\ CH{:}N.NHPh\end{array}$$

Glyoxalosazone



$$\begin{array}{l}CH{:}N.NHPh\\ |\\ CH{:}N.NHPh\end{array}$$

(E. Fischer, *l.c.*).

Formation.—The fact that phenylhydrazine reacts with aldehydes was first pointed out by

E. Fischer (*A.* 190, 134); thus with benzoic aldehyde:

$$Ph.CHO + H_2N.NHPh = Ph.CH{:}N.NHPh + H_2O.$$

Benzylidene-phenylhydrazine (Benzaldehydrazone)[1]

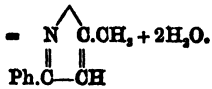
Later (*B.* 16, 661, footnote; 17, 572) he extended the reaction to ketones, diketones, ketonic acids, and carbonyl compounds generally, and proposed the use of phenylhydrazine as a reagent, analogous in its action to hydroxylamine, to be used in testing for the presence of carbonyl groups in compounds. At first (*B.* 17, 578) he recommended that the compound to be investigated should be heated with an aqueous solution of phenylhydrazine hydrochloride mixed with excess of sodium acetate, to which alcohol might be added to dissolve the compound; but later (*B.* 22, 90, footnote) a mixture of equal volumes of free phenylhydrazine and 50 p.c. acetic acid was substituted. The hydrazone generally separates as a sparingly soluble and frequently crystalline compound. The formation of a hydrazone under these circumstances is a proof that the compound under examination contains at least one carbonyl group in the ketonic or aldehydic form, *i.e.* attached with both its affinities to carbon atoms, or to a carbon and a hydrogen atom, or to two hydrogen atoms. Carbonyl groups attached with one or both affinities to oxygen or to nitrogen—as in $CO.OH$, $CO.NH_2$, &c.—do not react with phenylhydrazine. In some respects phenylhydrazine is to be preferred as a reagent to hydroxylamine: it is more readily obtained, and compounds containing more than one carbonyl group frequently react with two mols. of phenylhydrazine, thus showing the presence of two carbonyl groups, when they would only react with one mol. of hydroxylamine. The hydrazones of monocarbonyl compounds are formed like the aldehydrazones already mentioned: thus, *acetone-hydrazone* $(CH_3)_2C{:}N_2HPh$, and *phenylhydrazone-pyruvic acid* $CH_3.C(N_2HPh).COOH$. The action of phenylhydrazine on dicarbonyl compounds, however, varies with the relative positions of the two carbonyl groups. α-Dicarbonyl compounds, in which the two carbonyl groups are directly united, react either with one or with two mols. of phenylhydrazine, according to the proportions employed, to form respectively hydrazones and osazones; thus, diacetyl $CH_3.CO.CO.CH_3$ yields *diacetylmonohydrazone* $CH_3.C(N_2HPh).CO.CH_3$ and *diacetylosazone*

$$CH_3.C(N_2HPh).C(N_2HPh).CH_3$$

(v. Pechmann, *B.* 21, 1413). Glyoxal and benzil form similar osazones (Pickel, *A.* 232, 230). β-Dicarbonyl compounds, in which the two carbonyl groups are separated by a carbon atom, react with one mol. of phenylhydrazine to form an unstable hydrazone, which spontaneously parts with water yielding a *pyrazole*:

$$Ph.CO.CH_2.CO.CH_3 + Ph.NH.NH_2$$

Benzoylacetone



$$= \begin{array}{c} N.Ph \\ N \quad C.CH_3 \\ \| \quad\ \ \| \\ Ph.C{-}CH \end{array} + 2H_2O.$$

Methyl-diphenyl-pyrazole

This reaction does not, however, occur with β-diketones of the form $—CO.CR'_2.CO—$, in which both hydrogen atoms of the methylene group are replaced by alkyls (Fischer a. Bülow, *B.* 18, 2135; Knorr, *A.* 238, 139). γ-Dicarbonyl compounds, in which the two carbonyl groups are separated by two carbon atoms, react sometimes with 2 mols. of phenylhydrazine to form dihydrazones, thus:

$$CH_3.CO.CH_2.CH_2.CO.CH_3 + 2Ph.NH.NH_2 =$$

Acetonyl-acetone

$$CH_3.C(N_2HPh).CH_2.CH_2.C(N_2HPh).CH_3 + 2H_2O$$

(Paal, *B.* 18, 60), and sometimes with only 1 mol. of phenylhydrazine, eliminating, however, 2 mols. of water:

$$CH_3.CO.CH_2.CH_2.CO.C_6H_5 + C_6H_5.NH.NH_2$$

Acetonyl-acetophenone

$$= C_{17}H_{16}N_2 + 2H_2O.$$

The constitution of the compounds of the latter class is unknown (Paal, *B.* 17, 914).

Allusion has already been made to the similarity in the action of phenylhydrazine and of hydroxylamine on carbonyl compounds. The phenylhydrazo- group N.NHPh corresponds with the hydroximido- group N.OH. V. Meyer has shown that hydroximido- (isonitroso-) compounds are also formed by the action of nitrous acid on compounds containing the group CH_2 or CHR' attached to two electro-negative radicles, R′ being a readily displaceable radicle (acetyl or carboxyl). Japp and Klingemann (*C. J.* 1888, 523; *B.* 20, 3284 and 3398; 21, 549) have found that by the action of diazo- salts on compounds which yield hydroximido- compounds with nitrous acid (or on their sodium compounds) hydrazones are formed.[1] The following equations, in which for the sake of simplicity *free* diazobenzene is employed instead of a diazo- salt, will illustrate the analogy between the action of nitrous acid and diazo- salts on compounds of the above-mentioned type.

Thus with ethylic aceto-acetate the reactions may be expressed as follows:

$$CH_3.CO.CH_2.CO_2C_2H_5 + HNO_2$$
$$= CH_3.CO.C(N.OH).CO_2C_2H_5 + H_2O$$

Ethylic hydroximido-aceto-glyoxylate

and $$CH_3.CO.CH_2.CO_2C_2H_5 + Ph.N_2HO$$

Diazobenzene

$$= CH_3.CO.C(N_2HPh).CO_2C_2H_5 + H_2O.$$

Ethylic phenylhydrazone-aceto-glyoxylate

In the case of monalkyl derivatives of ethylic aceto-acetate, the acetyl group is expelled:

$$CH_3.CO.CH(CH_3).CO_2C_2H_5 + HNO_2$$
$$= CH_3.C(N.OH).CO_2C_2H_5 + C_2H_4O_2$$

Ethylic hydroximido-pyruvate

and $$CH_3.CO.CH(CH_3).CO_2C_2H_5 + Ph.N_2HO$$
$$= CH_3.C(N_2HPh).CO_2C_2H_5 + C_2H_4O_2.$$

Ethylic phenylhydrazone-pyruvate

With *free* aceto-acetic acid, or monalkyl-aceto-acetic acids, the carboxyl group is eliminated instead of the acetyl group:

$$CH_3.CO.CH_2.COOH + HNO_2$$
$$= CH_3.CO.CH{:}N.OH + CO_2 + H_2O$$

Pyruvaldehydroxime

and $$CH_3.CO.CH_2.COOH + Ph.N_2HO$$
$$= CH_3.CO.CH{:}N_2HPh + CO_2 + H_2O,$$

Pyruvaldehydrazone

---

[1] Abbreviation for 'benzaldehyde-hydrazone,' like 'benzaldoxim' for 'benzaldehyde-oxim.'

[1] Beyer and Claisen have, however, shown that in certain cases mixed azo- compounds are formed (*B.* 21, 1697).

whilst methaceto-acetic acid reacts with diazobenzene forming the monohydrazone of di-acetyl $CH_3.CO.C(N_2HPh).CH_3$ (*v. supra*) and ethaceto-acetic acid yields the corresponding compound of the formula $CH_3.CO.C(N_2HPh).C_2H_5$. Those of the foregoing hydrazones which contain a carbonyl group contiguous to the phenylhydrazone group may be made to react with phenylhydrazine to form osazones (J. a. K., *l.c.*).

Phenylhydrazine is capable of expelling the hydroximido- group to form hydrazones:

$$Ph_2C:N.OH + Ph.NH.NH_2$$

Diphenyl-acetoxime

$$= Ph_2C:N.NHPh + NH_2.OH$$

Benzophenone-phenylhydrazone

(Just, *B.* 19, 1206).

Properties.—A few of the hydrazones are liquid, but the majority are crystalline solids. By warming the solution of a carbonyl compound with phenylhydrazine and determining the melting-point of the hydrazone formed, the hydrazone, and thus the carbonyl compound from which it is derived, may frequently be identified. Many of the hydrazones decompose on melting; in determining the melting-point, therefore, the temperature must be raised as rapidly as is consistent with accuracy, otherwise too low a melting-point will be found (E. Fischer, *B.* 17, 573; 20, 827).

Reactions.—1. The hydrazones are readily reduced either with *sodium amalgam and acetic acid* or with *zinc-dust and acetic acid.* According to the length to which the reduction is carried the hydrazone either takes up two or four atoms of hydrogen—in the latter case with disruption of the molecule at the point of union of the nitrogen atoms. Thus phenylhydrazone-pyruvic acid $CH_3.C(N.NHPh).COOH$ yields in the first stage of reduction benzene-hydrazopropionic acid $CH_3.CH(NH.NHPh).COOH$ (E. Fischer a. Jourdan, *B.* 16, 2243), and this by further reduction breaks up into alanine $CH_3.CH(NH_2).COOH$ and aniline (Japp a. Klingemann, *C. J.* 1888, 535). This latter mode of reduction into a mixture of two bases was discovered by Tafel (*B.* 19, 1924), who proposed to employ the reaction as a method of preparing primary amines from carbonyl compounds; thus benzaldehyde could be converted, by the reduction of its hydrazone, into benzylamine.—2. The action of *heat* on the hydrazones has not been much studied. Many of them decompose when heated, yielding amongst other products aniline. When aldehydrazone is heated for some time to boiling it is partially converted into diacetyl-osazone (*v. supra*):

$$2CH_3.CH(N_2HPh)$$
$$= CH_3.C(N_2HPh).C(N_2HPh).CH_3 + H_2$$

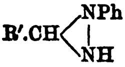
(Japp a. Klingemann, *C. J.* 1888, 542).—3. By the action of *sodium and an alkyl halogenide* on a hydrazone (Philips, *B.* 20, 2487), an alkyl group may be introduced; thus with benzaldehydrazone:

$$Ph.CH:N.N<\begin{matrix}Ph\\Na\end{matrix} + Ph.CH_2Cl$$

Sodium benzaldehydrazone

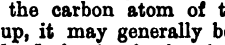
$$= Ph.CH:N.N<\begin{matrix}Ph\\CH_2.Ph\end{matrix} + NaCl;$$

and as the compound resulting in this case is identical with that obtained by the action of benzaldehyde on unsymmetrical benzyl-phenylhydrazine, it is thus proved that the hydrazones have the constitution $R'.CH:N.NHPh$ and not, as was otherwise conceivable, the constitution



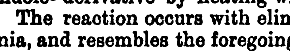
$$R'.CH<\begin{matrix}NPh\\|\\NH\end{matrix}$$

(Philips, *l.c.*). *Sodium alcoholates* may be substituted for sodium in the above reactions (Landsberg, *C. J.* 1888, 519).—4. By heating a hydrazone with an *anhydride of an organic acid* an acidoyl group may be introduced; thus, benzaldehydrazone, when heated with acetic anhydride, yields the compound $Ph.CH:N.N(C_2H_3O)Ph$ (Michaelis and Schmidt, *B.* 20, 1717 *n.*).—5. By heating hydrazones with *mineral acids* they may generally be hydrolysed into the carbonyl- compound and hydrazine from which they are derived (E. Fischer, *A.* 190, 135). The hydrazones of α-ketonic acids, however—thus, of pyruvic acid—are not hydrolysed by dilute mineral acids, whilst with strong acids they undergo complex decomposition (E. Fischer a. Jourdan, *B.* 16, 2243). Some secondary hydrazones are converted by hydrochloric acid into indole- derivatives, ammonia being eliminated in the process:



$$\begin{matrix}C_6H_5\\CH_3\end{matrix}>N.N:C<\begin{matrix}CH_3\\COOH\end{matrix}$$

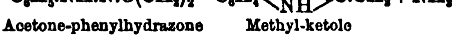
Methyl-phenylhydrazone-pyruvic acid



$$= C_6H_4\left\langle\begin{matrix}CH\\N-CH_3\end{matrix}\right\rangle C.COOH + NH_3$$

Methyl-indole-carboxylic acid

(E. Fischer a. Jourdan, *B.* 16, 2249; E. Fischer, *A.* 236, 116).—6. If a phenylhydrazone contain a methyl- or a methylene-group directly attached to the carbon atom of the original carbonyl-group, it may generally be converted into an indole- derivative by heating with zinc chloride. The reaction occurs with elimination of ammonia, and resembles the foregoing formation of an indole- derivative by the action of hydrochloric acid, but is applicable to primary as well as to secondary hydrazones:



$$C_6H_5.NH.N:C(CH_3)_2 = C_6H_4<\begin{matrix}CH\\NH\end{matrix}>C.CH_3 + NH_3$$

Acetone-phenylhydrazone Methyl-ketole

(E. Fischer, *A.* 236, 116). Aldehydrazone, however, when heated with zinc chloride, does not yield indole, but its homologues are converted into homologues of indole.

Some hydrazones undergo specific chemical changes, not general to the class, but depending on the presence of certain reactive groups in the molecule of the particular hydrazone. Such changes are, for example, the formation of a pyrazolone from the hydrazone of ethylic aceto-acetate and of pyrazolines from the hydrazones of unsaturated carbonyl- compounds (*v.* HYDRAZINES).

Osazones. As already mentioned, the name *osazone* denotes a compound containing in its molecule two dyad groups $NPhH.N{=}$ attached to two contiguous carbon atoms. E. Fischer (*B.* 17, 579) obtained from carbohydrates a series of characteristic compounds formed by the introduction of two phenylhydrazone groups into the molecule of a carbohydrate (*v. infra*). The compound from dextrose was termed *phenyl-glucosazone*; that from galactose, *phenyl-galactosazone*, and so on. Later, when it was found that in these compounds the two phenyl-hydrazine residues were in contiguous positions, the name *osazone* was applied to all compounds containing this particular grouping (E. Fischer, *B.* 21, 985).

Various methods for the preparation of osazones have already been incidentally mentioned in the course of this article. Thus, they are formed (1) by the action of 2 mols. of phenylhydrazine on an α-dicarbonyl compound; (2) by the action of 1 mol. of phenylhydrazine on a hydrazone containing a carbonyl-group contiguous to the hydrazone-group, such hydrazones being formed as intermediate products in the first-mentioned reaction; and (3) by heating an aldehydrazone. In addition to their formation by the foregoing reactions, which have been already described, osazones may be obtained (4) by heating iso-nitroso-ketones, in which the iso-nitroso- group is contiguous to the carbonyl-group, with phenyl-hydrazine:

$$\underset{\text{Isonitroso-acetone}}{CH_3.CO.CH(N.OH)} + 2Ph.NH.NH_2$$
$$= \underset{\text{Pyruvaldehyde-osazone}}{CH_3.C(N_2HPh).CH(N_2HPh)} + NH_2.OH$$

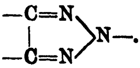
(v. Pechmann, *B.* 20, 2543). They are also formed (5) by the action of phenylhydrazine on compounds containing the group —CH(OH).CO—, thus, on α-ketone-alcohols and α-aldehyde-alcohols; and it is the members of the carbohydrate family belonging to these classes which yield osazones. In the cold—unless on long standing—only the carbonyl- group reacts with phenylhydrazine, and a hydrazone containing the group —CH(OH).C(N_2HPh)— is formed; but this compound, on heating with excess of phenylhydrazine, is converted into an osazone, the alcohol- group also taking part in the reaction. The mol. of hydrogen which is removed in this process reduces a mol. of phenylhydrazine to aniline and ammonia:

$$—CH(OH).CO— + 3NHPh.NH_2$$
$$= —C(N_2HPh).C(N_2HPh)—$$
$$+ NH_2Ph + NH_3 + 2H_2O$$

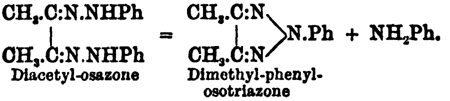
(E. Fischer, *B.* 17, 579; 20, 821; 21, 988, 2631). α-Dicarbonyl- compounds, on the other hand, react with excess of phenylhydrazine to form osazones *even in the cold.*

The osazones are of a yellow colour: the yellow colouring matters known as 'tartrazines' are the osazones of dihydroxytartaric acid. Conc. sulphuric acid dissolves the various osazones, giving characteristic colourations, and the solution generally exhibits some definite colour-change on standing (Japp a. Klingemann, *B.* 21, 549). Fuming hydrochloric acid hydrolyses the osazones in the cold into phenylhydrazine and the α-dicarbonyl- compound from which they are derived (E. Fischer, *B.* 21, 2631).

Osotriazones. The osotriazones contain the closed-chain complex

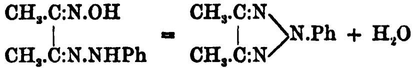


They are formed: 1. From the osazones either by boiling with dilute acids (v. Pechmann, *B.* 21, 2758), or by heating (Auwers a. V. Meyer, *B.* 21, 2806), the latter process giving the better yield:



Diacetyl-osazone Dimethyl-phenyl-osotriazone

2. From a hydrazone-hydroxim by the action of the chlorides of phosphorus:



Diacetyl-hydrazone-hydroxim

(v. Pechmann, *l.c.*).—3. From the osotetrazones (*v. infra*).

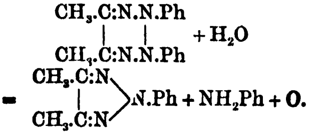
The osotriazones are feebly basic, very stable compounds.

Osotetrazones. The osotetrazones contain the closed-chain complex $\begin{array}{c}—C{=}N—N—\\ |\qquad\quad |\\ —C{=}N—N—\end{array}$. They are obtained by oxidising the osazones with potassium dichromate in dilute acetic acid solution:

$$\underset{\text{Diacetyl-osazone}}{\begin{array}{l}CH_3.C{:}N.NHPh\\ \;\;|\\ CH_3.C{:}N.NHPh\end{array}} + O = \underset{\text{Diacetyl-osotetrazone}}{\begin{array}{l}CH_3.C{:}N.N.Ph\\ \;\;|\qquad\;\; |\\ CH_3.C{:}N.N.Ph\end{array}} + H_2O$$

(v. Pechmann, *B.* 21, 2755). They are dark-red neutral compounds, the formation of which has been recommended as a characteristic test for the osazones (v. P.).

By boiling the osotetrazones with dilute hydrochloric acid they are converted into osotriazones:



Dimethyl-phenyl-osotriazone

The oxygen is not liberated, but oxidises a portion of the substance (v. Pechmann, *B.* 21, 2757).

Neither the osotriazones nor the osotetrazones have been much studied. F. R. J.

HYDRAZOPHENINE $C_{36}H_{31}N_5$. [174°]. Formed by heating azophenine with alcoholic ammonium sulphide at c. 140°. Colourless needles (O. Fischer a. Hepp, *B.* 20, 2483).

HYDRAZO-PHENOL *v.* Di-oxy-di-phenyl-hydrazine.

HYDRAZO-DIPHENYL $C_6H_5.C_6H_4.NH.NH.C_6H_4.C_6H_5$. *Di-diphenyl hydrazine.* [247°]. Prepared by reducing azoxy-diphenyl with alcoholic ammonium sulphide (Zimmermann, *B.* 13, 1961). White pearly plates, insol. water, sl. sol. alcohol and HOAc, m. sol. ether.

HYDRAZO-PHENYL-METHYL *v. s*-Phenyl-methyl-hydrazine.

HYDRAZO-TEREPHTHALIC ACID *v.* Di-phenyl-hydrazine tetra-carboxylic acid.

HYDRAZO-TOLUENE *v.* Di-tolyl-hydrazine.

HYDRAZO-TOLUIDINE *v. Di-amido-*di-tolyl-hydrazine.

HYDRAZO-XYLENE v. Di-xylyl-hydrazine.

HYDRAZULMIN v. Azulmic acid.

HYDRIDES. Binary compounds of hydrogen. Hydrogen forms binary compounds with all the distinctly non-metallic elements, also with As and Sb. A hydride of Cu is known, and there probably exists a definite but unstable hydride of Pd, and perhaps of one or two of the other platinum metals. There are also indications of the existence of hydrides of K and Na.

The non-metallic hydrides may be classified in accordance with their composition as follows:—

(i.) *HM*: HF, HCl, HBr, HI.
(ii.) H_2M: H_2O, H_2S, H_2Se, H_2Te.
(iii.) H_3M: H_3N, H_3P, ? H_3B, H_3As, H_3Sb.
(iv.) H_4M: H_4C, H_4Si.
(v.) *Various*: H_2O_2, ? H_2S_2, H_4P_2, H_4N_2; numerous hydrocarbons.

A definite hydride of Cu, Cu_2H_2, has been obtained. It decomposes at 60° into Cu and H. K and Na absorb H rapidly at c. 300°; compounds, K_2H and Na_2H, appear to be formed. Pd, Pt, Fe, Ni, Au, and some other metals, when used as the negative electrodes in the electrolysis of water, absorb considerable quantities of H. A compound Pd_2H is probably formed. In the other cases it is doubtful whether the absorption is purely physical, or partly chemical and partly physical. As a class, the metals do not form definite hydrides, while the non-metals do form hydrides. The greater number of the non-metallic hydrides may be produced by direct union of their elements; a few are produced by evolving H in contact with solutions of compounds of the elements, *e.g.* AsH_3, and a few by more indirect methods.

The non-metallic hydrides vary much in properties: HCl, HBr, and HI are strong acids; H_2S is a very weak acid; NH_3 is markedly alkaline; PH_3 is feebly alkaline; H_2O is neutral; hydrocarbons differ extremely in their properties, although none is either distinctly an acid or an alkali. Some hydrides are easily decomposed by heat, *e.g.* H_2O_2, HI; others are extremely stable as regards the action of heat, *e.g.* HCl, H_2O. M. M. P. M.

HYDRINDIC ACID is α-oxy-*o*-amido-phenyl-acetic acid, of which di-oxindole is the anhydride.

HYDRINDINE v. Indine.

HYDRINDONAPHTHENE v. Indonaphthene dihydride.

HYDRIODIC ACID v. Iodhydric acid, vol. iii.

HYDRO-. Organic compounds whose names begin with this prefix will usually be found described as hydrides of the substances to whose names it is attached.

Use of this prefix applied to inorganic acids and salts. For *hydro- acids* and *hydro- salts* v. the acids or salts sought for. Thus, *hydrofluoboric acid* will be found under Borofluorhydric acid; *hydroferrocyanic acid* will be found under Ferrocyanhydric acid; *hydrofluosilicates* will be found under Silicates.

HYDRO-ACRIDINE v. Acridine octohydride.

HYDRO-ANISOÏN $C_6H_4(OMe).CH(OH).CH(OH).C_6H_4OMe$. *Di-methoxy-hydro-benzoïn.* [170°–172°]. A small quantity of this body is formed from anisic aldehyde in ethereal solution by sodium amalgam (C. Saytzeff, *Z.* [2] 3, 678; Samosadsky, *Z.* [2] 4, 644; Rossel, *Z.* [2] 5, 562; M. Wallach, *A.* 226, 78). Pyramids, v. sl. sol. warm water, m. sol. ether, v. sol. hot alcohol. When distilled in a current of CO_2 it partly sublimes, and is partly converted into anisic aldehyde. Conc. HNO_3 forms nitro-anisic aldehyde. Chromic acid mixture gives anisic acid. PCl_5 forms $C_6H_4(OMe).CO.Cl$.

Isohydroanisoïn $C_{16}H_{18}O_4$. [125°]. Separates only after the addition of water to the alcoholic solution of anisic aldehyde which has been treated with sodium. Slender interlacing needles, v. e. sol. alcohol and ether.

Deoxyanisoïn $C_{16}H_{16}O_3$. [95°]. Formed by boiling hydro-anisoïn or iso-hydro-anisoïn with dilute H_2SO_4. Tufts of needles, v. sol. alcohol and ether. Oxidised by chromic acid mixture to anisic aldehyde and anisic acid.

Isomeride of Deoxyanisoïn $C_{16}H_{16}O_3$. [215°]. Formed by the action of Zn and HCl on hydro-anisoïn or on anisic aldehyde. Crystalline; insol. ether.

HYDRO-ANTHRACENE v. Anthracene hydride. A hydride $C_{14}H_{24}$ [88°] (c. 270°) has been obtained by Lucas (*B.* 21, 2510) by heating anthracene (3 g.) with red phosphorus (3 g.) and HI (16g. of S.G. 1·7) for twelve hours at 250°.

HYDRO-ANTHRACENE CARBOXYLIC ACIDS v. vol. i. p. 278.

HYDRO-ANTHRANOL v. Anthranol dihydride, vol. i. p. 279.

HYDRO-APO-ATROPINE v. Atropine.

HYDRO-ATROPIC ACID v. α-Phenyl-propionic acid.

HYDROBENZAMIDE v. Benzoic aldehyde.

HYDRO-BENZENE DI-CARBOXYLIC ACIDS v. *Hydrides* of the Phthalic acids.

HYDROBENZOIC ACID v. Benzoleïc acid.

HYDROBENZOÏN $C_{14}H_{14}O_2$ *i.e.* $C_6H_5.CH(OH).CH(OH).C_6H_5$. *Stilbene alcohol.* Mol. w. 214. [138°] (Paal, *B.* 16, 637); [134°] (Zincke); [133°] (A.). (above 300°). S. ·25 at 15°; 1·25 at 100°.

Formation.—1. By the action of granulated zinc upon benzoic aldehyde dissolved in alcohol which has previously been partially saturated with HCl. The hydrobenzoïn is ppd. on subsequent addition of water (Zinin, *A.* 123, 125).—2. Together with isohydrobenzoïn and benzyl alcohol by the action of sodium-amalgam on benzoic aldehyde dissolved in alcohol (Ammann, *Z.* [2] 7, 83; *A.* 168, 69).—3. From benzoïn by heating with alcoholic potash at 155° in an exhausted tube, benzilic acid being also formed (Zinin, *Bl.* [2] 7, 260).—4. By the action of sodium-amalgam on benzoïn (Grimaux, *B.* 2, 281) or on benzil (Forst a. Zincke, *A.* 182, 259).—5. From $C_6H_5.CHBr.CHBr.C_6H_5$ by treatment with silver acetate or oxalate and saponification of the product (Limpricht a. Schwanert, *Z.* [2] 3, 684; *A.* 160, 177).

Properties.—Silky needles (from water or dilute alcohol) or monoclinic tables (from absolute alcohol); v. sol. alcohol.

Reactions.—1. *Nitric acid* oxidises it to benzoïn and finally to benzil (Zinin).—2. *Chromic acid mixture* forms benzoic aldehyde (Zincke, *A.* 198, 121).—3. PCl_5 forms (α)- and (β)-di-chloro-di-phenyl-ethane $C_6H_5CHCl.CHCl.C_6H_5$. 4. PBr_5 forms in like manner a bromide

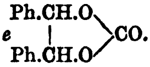
$C_{14}H_{12}Br_2$.—5. Dilute H_2SO_4 at 200° forms di-phenyl-acetic aldehyde and an anhydride $C_{14}H_{12}O$ (Breuer a. Zincke, *B.* 11, 72; Weise, *A.* 248, 34).

Acetyl derivative $C_6H_5.CH(OAc).CH(OH).C_6H_5$. [84°]. From hydrobenzoïn and HOAc at 180° (Limpricht a. Schwanert, *A.* 160, 190; Forst a. Zincke, *A.* 182, 254). Long needles (from aqueous HOAc), v. e. sol. alcohol, ether, and HOAc.

Di-acetyl derivative $(C_6H_5)_2C_2H_2(OAc)_2$: [135°]; formed by acetylation of hydrobenzoïn, or by the action of zinc-dust on a mixture of benzoic aldehyde and acetyl chloride (Paal, *B.* 16, 636). Formed also from di-bromo-di-phenyl-ethane $C_6H_5.CHBr.CHBr.C_6H_5$ and AgOAc (Limpricht a. Schwanert, *A.* 160, 177). Monoclinic prisms (from ether); m. sol. cold alcohol, sol. ether and benzene. PCl_5 converts it into (*a*)-di-chloro-di-phenyl-ethane $C_6H_5.CHCl.CHCl.C_6H_5$.

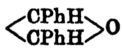
Benzoyl derivative $C_6H_5.CH(OH).CH(OBz).C_6H_5$. [161°]. Formed, together with the di-benzoyl derivative by heating hydrobenzoïn (1 pt.) with Bz_2O (3 pts.) at 160° (Forst a. Zincke, *A.* 182, 277). Needles or plates (from alcohol); v. sol. alcohol, ether, and chloroform.

Di-benzoyl derivative Ph.CH(OBz).CH(OBz).Ph. [246°]. Small white needles, sl. sol. most solvents. Formed, together with the di-benzoyl compound of isohydrobenzoïn, by the action of zinc-dust on a mixture of benzoic aldehyde and benzoyl chloride (Paal, *B.* 17, 909). Formed also by treating the compound PhCHBr.CHBrPh with AgOBz (Forst a. Zincke, *A.* 182, 277).

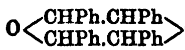
Carbonyl derivative 

$$\begin{matrix} Ph.CH.O \\ | \\ Ph.CH.O \end{matrix}\!\!>\!CO.$$

[126°]. Obtained by the action of $ClCO_2Et$ on the sodium derivative of hydrobenzoïn, which is itself got by heating hydrobenzoïn in benzene solution with sodium-amalgam (Wallach, *A.* 226, 81). Needles (from alcohol). Saponified by alcoholic KOH.

Anhydride $C_{14}H_{12}O$ *i.e.* 

$$<\!\begin{matrix} CPhH \\ CPhH \end{matrix}\!>O$$

or 

$$O<\!\begin{matrix} CHPh.CHPh \\ CHPh.CHPh \end{matrix}\!>O.$$

Di-phenyl-ethylene oxide. [132°]. Formed by boiling hydrobenzoïn with dilute (20 p.c.) sulphuric acid, distilling off di-phenyl-acetic aldehyde and extracting the residue with ether. Monoclinic crystals (from ether). Not volatile with steam. Insol. water, v. sol. benzene, HOAc, and hot alcohol. At 250° it splits up into *s*-di-phenyl-ethylene and benzoic aldehyde. *Reactions.*—1. When heated for 17 hours with Bz_2O at 240° it gives di-benzoyl hydrobenzoïn and some *s*-di-phenyl-ethylene.—2. HOAc at 170° forms di-acetyl-hydrobenzoïn.—3. Ac_2O does not act below 240°, at which temperature it gives di-acetyl-hydrobenzoïn, *s*-di-phenyl-ethylene, and benzoic aldehyde.—4. BzCl gives (*a*)-di-chloro-di-phenyl-ethane Ph.CHCl.CHCl.Ph [192°]. PCl_5 forms the same body.—5. By heating for 8 hours at 200° with conc. HIAq and phosphorus it is reduced to *s*-di-phenyl-ethane [52°].—6. CrO_3 in HOAc forms $C_{28}H_{22}O_3$, which crystallises from hot alcohol in small felted needles [155°] and $C_{15}H_{11}O_2$ [145°] (Breuer a. Zincke, *A.* 198, 169).—7. Dilute (20 p.c.) H_2SO_4 at 200° forms di-phenyl-acetic aldehyde.—8. HClAq (S.G. 1·19) at 170° gives di-phenyl-acetic aldehyde and (*a*)-di-chloro-di-phenyl-ethane.

Isohydrobenzoïn $C_{14}H_{14}O_2$ *i.e.* $C_6H_5.CH(OH).CH(OH).C_6H_5$. [120°]. S. ·19 at 15°; 1·25 at 100°. Formed, together with a smaller quantity of hydrobenzoïn, when sodium-amalgam acts on benzoic aldehyde in presence of water. The presence of alcohol diminishes the proportion of isohydrobenzoïn to hydrobenzoïn (Ammann a. Fittig, *A.* 168, 70). The separation may be effected by repeated crystallisation from alcohol, in which isohydrobenzoïn is somewhat the more soluble. Formed also by saponifying its di-acetyl derivative. Glistening hydrated needles (from water), anhydrous hexagonal crystals (from alcohol), or monoclinic prisms (from ether). The hydrated crystals melt at 96°. V. sol. alcohol, ether, and chloroform.

Reactions.—1. PCl_5 gives (*a*)-di-chloro-di-phenyl-ethane Ph.CHCl.CHCl.Ph [184°], and a resinous compound $C_{28}H_{23}ClO$ [150°] (Breuer a. Zincke, *A.* 198, 167).—2. Boiling dilute H_2SO_4 forms di-phenyl-acetic aldehyde and the anhydride $C_{14}H_{12}O$ [102°].—3. By heating with Bz_2O there is formed mono- and di-benzoyl-isohydrobenzoïn and also di-benzoyl hydrobenzoïn.

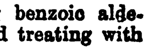
Sodium derivative Ph.CH(ONa).CH(ONa)Ph (?). In an ethereal solution of isohydrobenzoïn sodium-amalgam forms a powdery sodium derivative. Some of the isohydrobenzoïn appears to be changed at the same time into a crystalline isomeride [125°], which is slowly dissolved by boiling water, being changed to isohydrobenzoïn.

Acetyl derivative $C_6H_5.CH(OH).CH(OAc).C_6H_5$. [88°]. Formed by the action of KOAc or of AgOAc on Ph.CHBr.CHBr.Ph (Forst a. Zincke, *A.* 182, 282). Short thick needles.

Di-acetyl derivative $C_6H_5.CH(OAc).CH(OA\ ).C_6H_5$. [118°]. Formed by digesting isohydrobenzoïn with acetyl chloride for 24 hours. Formed also by boiling Ph.CHBr.CHBr.Ph (1 pt.) dissolved in HOAc (3 pts.) with an excess of KOAc for 12 hours (Zincke, *A.* 182, 262; 198, 154). Plates (from alcohol). Occurs sometimes in trimetric prisms [106°]. V. sol. alcohol, ether, and chloroform.

Benzoyl derivative $C_6H_5.CH(OH).CH(OBz).C_6H_5$. [130°]. Formed, together with the di-benzoyl derivative, by heating isohydrobenzoïn with excess of Bz_2O at 160° (Forst a. Zincke, *A.* 182, 285). Small needles (from dilute alcohol). V. e. sol. alcohol, ether, and chloroform.

Di-benzoyl derivative $C_{14}H_{12}(OBz)_2$: [151°]; fine silky needles; v. e. sol. ordinary solvents. Formed, together with the di-benzoyl derivative of hydro-benzoïn, by the action of zinc-dust on a mixture of benzoic aldehyde and benzoyl chloride (Paal, *B.* 17, 909). Formed also, together with its isomeride, by heating isohydrobenzoïn with Bz_2O; also by the action of Ph.CHBr.CHBr.Ph on AgOBz.

Carbonyl derivative 

$$\begin{matrix} Ph.CH.O \\ Ph.CH.O \end{matrix}\!>\!CO.$$

[110°]. Prepared by dissolving benzoic aldehyde and $Cl.CO_2Et$ in ether and treating with sodium amalgam. A violent reaction occurs;

when it abates the flask is heated for some time with inverted condenser. The liquid is filtered and evaporated, the residue is crystallised from alcohol. The yield is bad. Formed also by treating the sodium derivative of isohydrobenzoïn in ether or benzene with $ClCO_2Et$, an intermediate body $Ph.CH(OCO_2Et).CH(OCO_2Et).Ph$ being perhaps formed. Monoclinic plates (from alcohol). Insol. cold water, sl. sol. boiling water. Sl. sol. cold alcohol or ether. Insol. CS_2, sol. benzene. Decomposed by boiling potash into potassium carbonate and iso-hydro-benzoïn. It is not affected by Ac_2O. PCl_5 converts it into (*a*)-di-chloro-*s*-di-phenyl-ethane [186°] (Wallach, *J. pr.* [2] 25, 262; *A.* 226, 80).

Anhydride $C_{14}H_{12}O$. [102°]. Formed, like the corresponding anhydride of hydrobenzoïn, by boiling isohydrobenzoïn with dilute H_2SO_4 (Zincke a. Breuer). Monoclinic crystals (from ether). More soluble in alcohol than its isomeride.

Reactions.—1. When heated with Bz_2O it gives *s*-di-phenyl-ethylene and di-benzoyl-isohydrobenzoïn.—2. HOAc has no action even at 250°.—3. Ac_2O does not act at 170°.—4. BzCl yields Ph.CHCl.CHCl.Ph [192°]. PCl_5 forms a compound $C_{28}H_{23}ClO$, which is finally converted into Ph.CHCl.CHCl.Ph.—5. HIAq and P at 200° form *s*-di-phenyl-ethane [52°].—6. CrO_3 in HOAc acts upon it in the same way as upon its isomeride.

HYDROBENZOÏN-DI-*p*-CARBOXYLIC ACID $C_{16}H_{14}O_6$ *i.e.* $C_6H_4(CO_2H).CH(OH).CH(OH).C_6H_4(CO_2H)$. Obtained by reduction of the sodium salt of benzoïn-di-carboxylic acid with sodium-amalgam. Infusible. Unsublimable (Oppenheimer, *B.* 19, 1817).

HYDROBERBERINE *v.* Berberine.

HYDROBROMIC ACID *v.* Bromhydric acid, vol. i. p. 532.

HYDRO-BROMO-CINCHENE *v.* Cinchene bromohydride.

HYDRO-BROMO-CINCHONINE *v.* Cinchonine bromohydride.

HYDROBUTYRAMIDE *v.* Isobutyric aldehyde.

HYDROBUTYROFURONIC ACID $C_9H_{14}O_5$ *i.e.* $CO_2H.CH_2.CH_2.CO.CH_2.CH_2.CH_2.CH_2.CO_2H$. An indistinctly crystalline acid formed by reducing butyro-furonic acid $C_9H_{12}O_5$ with sodium-amalgam (Tönnies, *B.* 12, 1201).—Ag_2A''.

HYDRO-CAFFURIC ACID *v.* Caffeïne.

HYDROCAMPHENE *v.* Decinene.

HYDROCARBONS. Compounds containing carbon and hydrogen only. Liquid hydrocarbons, especially terpenes $C_{10}H_{16}$ and their isomerides, are commonly found in essential oils from plants; solid hydrocarbons have been obtained from the fruit of *Heracleum Sphondylium*, *H. giganteum*, *Pastinaca sativa*, and from other plants (Guthzeit, *B.* 21, 2881). The chief source of hydrocarbons is, however, the dry distillation of organic bodies, the nature of the product depending upon the temperature at which the distillation takes place, since a red heat tends to deprive hydrocarbons of a part of their hydrogen. Thus when coal is distilled at the lowest possible temperature, the distillate consists chiefly of paraffins and olefines; while distillation at a bright-red heat forms large quantities of aromatic hydrocarbons. American petroleum, formed by the slow decomposition of vegetable matter under the surface of the earth, probably at a moderate temperature, is very largely composed of paraffins (*cf.* Engler, *B.* 21, 1816).

The hydrocarbons are insoluble in water; they are neutral, and do not form salts with acids or alkalis; they are not saponified by boiling with dilute acids or alkalis, and are for the most part not affected by that treatment. They do not unite with alkaline bisulphites, nor do they react with hydroxylamine or phenyl hydrazine.

According to Berthelot (*C. R.* 84, 714) when liquid hydrocarbons are decomposed by passing powerful induction sparks through them the gases given off consist of hydrogen, methane, ethane, ethylene, and acetylene, but no hydrocarbon of higher molecular weight; carbon is deposited in the case of terpenes and aromatic hydrocarbons, but not from paraffins.

The hydrocarbons with which bromine combines even in the dark are known as unsaturated fatty hydrocarbons; the remaining hydrocarbons may be divided into saturated fatty hydrocarbons and aromatic hydrocarbons, which may be distinguished by treatment with fuming nitric acid, which forms nitro- derivatives with aromatic hydrocarbons, but never does so with the saturated fatty hydrocarbons.

The saturated fatty hydrocarbons are also called paraffins, and contain a larger percentage of hydrogen than any other hydrocarbons; they may be included in the general formula C_nH_{2n+2}. Unsaturated fatty hydrocarbons of the formula C_nH_{2n} are called olefines, since olefiant gas is the first member of the series. Of the hydrocarbons C_nH_{2n-2} those which give pps. with ammoniacal solutions of cuprous chloride and of silver nitrate are held to contain the group C:CH and belong to the acetylene series.

Vowel nomenclature, first proposed by Laurent in naming the chlorinated derivatives of naphthalene, was adopted by Hofmann to distinguish the different classes of hydrocarbons. Thus, according to Hofmann, the names of the compounds:

C_nH_{2n+2}	end in	– ane
C_nH_{2n}	„	– ene
C_nH_{2n-2}	„	– ine
C_nH_{2n-4}	„	– one
C_nH_{2n-6}	„	– une.

Inasmuch as *ine* is the usual termination of bases, and *one* that of ketones, in this dictionary the names of unsaturated hydrocarbons have been made to end in *ene*, thus:

Hydrocarbons	C_nH_{2n}	end in	– ylene
„	C_nH_{2n-2}	„	– inene
„	C_nH_{2n-4}	„	– onene
„	C_nH_{2n-6}	„	– unene.

Paraffins. The saturated fatty hydrocarbons or paraffins are named as follows:

Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}
Heptane	C_7H_{16}
Octane	C_8H_{18}

Ennane or Nonane	C_9H_{20}
Decane	$C_{10}H_{22}$
Hendecane or Undecane	$C_{11}H_{24}$
Dodecane	$C_{12}H_{26}$
Tridecane	$C_{13}H_{28}$
Tetradecane	$C_{14}H_{30}$
Pentadecane	$C_{15}H_{32}$
Hexadecane	$C_{16}H_{34}$
Heptadecane	$C_{17}H_{36}$
Octodecane	$C_{18}H_{38}$
Enndecane	$C_{19}H_{40}$
Icosane	$C_{20}H_{42}$
Henicosane	$C_{21}H_{44}$
Do-icosane	$C_{22}H_{46}$
Tri-icosane	$C_{23}H_{48}$
. . . .	
Triacontane	$C_{30}H_{62}$.

From a structural point of view any paraffin may be regarded as formed from the next lower homologue by displacement of H by CH_3. As the hydrogen atoms in methane are similarly situated there can be only one ethane, and as the atoms of hydrogen in ethane $CH_3.CH_3$ are similarly situated there can be only one propane. But in propane $CH_3.CH_2.CH_3$ it is possible to displace a hydrogen atom either in the methylene group CH_2 or in one of the two methyl groups; thus we arrive at two butanes: $CH_3.CH(CH_3).CH_3$ and $CH_3.CH_2.CH_2(CH_3)$.

Proceeding in this way we find that there are theoretically possible 3 pentanes, 5 hexanes, 9 heptanes, 18 octanes, 35 ennanes, 75 decanes, 159 hendecanes, 355 dodecanes, 802 tridecanes, &c.

The paraffins are said to be normal when they contain only two methyl groups, and may consequently be represented by a chain that has no branches, *e.g.* $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$. The boiling-points of the normal paraffins are:

Pentane (37°)
Hexane (70°)
Heptane (99°)
Octane (124°),

after which they rise 19° for each increment of CH_2. The other paraffins boil at lower temperatures than their normal isomerides.

Occurrence.—Among the products of the destructive distillation of coal, bituminous shale, peat, &c., and in American petroleum. Natural or artificial petroleum yields on distillation: (*a*) petroleum ether or ligroïn boiling from 35° to 90°, containing chiefly pentane, hexane, and heptane; (*b*) benzoline or petroleum spirit, boiling from 90° to 150° and containing heptane, octane, and ennane; (*c*) kerosene, petroleum-naphtha, or paraffin oil boiling from 150° to 200°, containing decane, hendecane, and dodecane; (*d*) solid paraffin wax, a mixture of saturated hydrocarbons of still higher molecular weight (Greville Williams, *Tr.* 1857, 737; *C. J.* 15, 130; Schorlemmer, *C. J.* 15, 419; Pelouze a. Cahours, *A.* 124, 289; 127, 196; 129, 87).

Formation.—1. By distilling the acids $C_nH_{2n}O_2$ with excess of potash, lime, or baryta. 2. By the action of water on the zinc alkyls; this reaction may be carried out by simply heating the alcoholic iodide with zinc and water, or by treating them with the copper-zinc couple in presence of water or alcohol.—3. By the reduction of the chlorides or iodides of alcohol radicles by zinc and hydrochloric acid, by HI, or by sodium-amalgam.—4. By the action of sodium or of reduced silver on an iodide or mixture of iodides $RI + R'I + Na_2 = 2NaI + RR'$. This process is known as Wurtz's reaction (Wurtz, *A. Ch.* [3] 44, 275).—5. By the action of alcoholic iodides on zinc-alkyls.—6. By the electrolysis of the sodium salts of the fatty acids.

Properties.—Methane, ethane, propane, and butane are gaseous at ordinary temperatures; the specific gravity of the higher paraffins in the liquid state steadily rises with increasing molecular weight. The paraffins are distinguished by their chemical indifference (*parum affinis*). They are not attacked by KOH, by H_2SO_4, or by cold fuming HNO_3.

Reactions.—1. *Chlorine* acting on a normal paraffin forms only primary and secondary chlorides, the latter containing the group $CHCl.CH_3$. Bromine forms, however, only secondary bromides of similar constitution (Schorlemmer). The isomeric mono-chlorinated paraffins got from petroleum yield, by abstracting HCl, a mixture of olefines one portion of which combines readily with cold HCl, whilst the rest only combines on heating. The chloro- derivatives formed in the cold distil with partial decomposition and at a lower temperature than those formed by heating. The latter distil without decomposition and have the general formula $CH_3.CHCl\,C_nH_{2n+1}$ (Schorlemmer, *C. J.* 26, 319; *Pr.* 29, 364; *T.* 171, 451; Morgan, *C. J.* 28, 301; Le Bel, *Bl.* [2] 28, 460).—2. *Bromine* does not act upon them in the dark, in sunlight its colour disappears, a molecule of HBr being formed for each molecule of bromine used up.—3. *Hypochlorous acid* does not unite with paraffins.—4. *Chromic acid* and hot nitric acid (S.G. 1·4 to 1·5) oxidise them to CO_2, forming in some cases intermediate fatty acids (Schorlemmer, *Pr.* 16, 373).

Olefines C_nH_{2n}. The names of the olefines are:—

Ethylene	C_2H_4
Propylene	C_3H_6
Butylene	C_4H_8
Amylene	C_5H_{10}
Hexylene	C_6H_{12}

The higher members are named by writing -ylene in place of the -ane in the names of the paraffins (*v. supra*). Methylene CH_2 does not appear capable of existing; in reactions where it might be expected ethylene is formed instead. It will be observed that the olefines have all the same percentage composition. The hydrocarbons in Caucasian petroleum, although isomeric with the olefines, appear to be hexahydrides of the homologues of benzene (Markownikoff, *B.* 20, 1850).

Formation. — 1. By dehydration of the saturated fatty monohydric alcohols $C_nH_{2n+2}O$. This may be done by means of H_2SO_4, $ZnCl_2$, or P_2O_5. In the case of the higher alcohols a mixture of hydrocarbons is, however, produced. 2. By the action of alcoholic KOH on the alkyl iodides.—3. By passing alkyl chlorides over red-hot lime. In some cases mere distillation is sufficient to split up the alkyl chlorides into olefine and HCl.—4. A large number of olefines are produced in the manufacture of illuminating gas from oil (Armstrong, *C. J.* 49, 74).—5. By the electrolysis of the alkaline salts of dibasic fatty acids.

Reactions.—1. The olefines combine readily with *chlorine*, *bromine*, and *iodine* forming oily compounds (*e.g.* Dutch liquid); hence their name.—2. They combine with SO_3, and are therefore absorbed by Nordhausen sulphuric acid. Conc. H_2SO_4 forms alkyl sulphuric acids.—3. They combine with HCl, HBr, and HI. Conc. HIAq, however, at 100°, soon reduces them to paraffins. Olefines of the formula CH_2:CHR combine with HCl only on heating (Le Bel, *Bl.* [2] 28, 460). Those of the formulæ CH_2:CRR′ or CHR:CHR′ combine with cold HCl (Le Bel; *cf.* Schorlemmer a. Thorpe, *A.* 217, 151).—4. Alkaline $KMnO_4$ oxidises them to oxalic, acetic, formic, carbonic, and other acids (Berthelot, *C. R.* 64, 35).—5. Many olefines may be oxidised by CrO_3 to aldehydes or ketones (Berthelot, *C. R.* 68, 334).—6. HClO unites forming chlorhydrins of dihydric alcohols or glycols. A very simple method of preparing hypochlorous acid for employment in the preparation of organic chlorhydrins consists in acidifying a solution of bleaching powder with boric acid. The theoretical quantity of the unsaturated organic compound is then added, allowed to stand for some time in the dark, and the chlorhydrin extracted with ether (Lauch, *B.* 18, 2287).—7. The olefines are prone to polymerisation especially in presence of $ZnCl_2$ or H_2SO_4.

Acetylene series C_nH_{2n-2}. The hydrocarbons C_nH_{2n-2} may be divided into (*a*) acetylenes proper: R.C:CH; (*b*) dialkyl-acetylenes: RC⋮CR′; (*c*) di-ethylenic hydrocarbons: RCH:CH.CH:CHR′; and (*d*) isoallylenes: RR′C:C:CR″R‴ (*cf.* Béhal, *A. Ch.* [6] 15, 268).

Formation.—1. By heating bromo-olefines, or the dibromides of olefines with alcoholic potash. Thus they may readily be obtained from aldehydes and ketones by successive treatment with PCl_5 and alcoholic potash.—2. By electrolysis of the sodium salt of unsaturated dibasic acids.—3. In the destructive distillation of organic bodies, and in the incomplete combustion of coal-gas.

Reactions.—1. The hydrocarbons RC⋮CH form pps. in ammoniacal solutions of cuprous chloride and of silver nitrate. These pps. are decomposed by HCl with liberation of the hydrocarbon.—2. They combine with either one or two molecules of bromine, HCl, HBr, HI, and HOCl.—3. By successive treatment with H_2SO_4 and water they can be hydrated; acetylene changing to aldehyde, and allylene to acetone.—4. The hydrocarbons RC⋮CH give pps. in an aqueous solution of $HgCl_2$; when the product is treated with acids aldehydic or ketonic products of hydration are liberated (Kutscheroff, *B.* 17, 13).—5. A saturated alcoholic solution of $AgNO_3$ gives crystalline pps. with acetylenic hydrocarbons; thus heptinene gives $C_7H_{11}AgAgNO_3$ which deflagrates when heated (Béhal, *A. Ch.* [6] 15, 423).—6. $KMnO_4$ and chromic acid attack the hydrocarbons at the unsaturated point; thus diallyl gives CO_2 and succinic acid. Béhal (*A. Ch.* [6] 16, 368) thinks that no hydrocarbon of the isoallylene type has as yet been isolated. Thus by heating CH_2Cl.CH:CHCl in dry benzene with sodium he failed to obtain isoallylene. He was equally unable to obtain CH_2:C:CH_2 by heating CH_2Cl.CCl:CH_2 with sodium; while allyl iodide heated with PbO in excess only gave propylene; and by heating with HgO, CuO, or Ag_2O at 125°-150°, CO is formed, but no isoallylene. When allyl alcohol is dehydrated by P_2O_5 no trace of isoallylene is obtained, the products being ethylene and propylene. Ethyl allyl oxide behaves in like manner, the decomposition proceeding with greater regularity (Béhal, *A. Ch.* [6] 16, 360). According to Gustavson (*J. pr.* [2] 38, 203), however, isoallylene can be obtained by the action of zinc-dust on di-bromo-propylene CH_2Br.CBr:CH_2 in presence of alcohol. He describes it as a gas which unites with bromine forming $C_3H_4Br_2$, and which, when treated with H_2SO_4 and water successively, yields acetone.

Benzene series C_nH_{2n-6}. The hydrocarbons of this series are named as follows:—

Benzene C_6H_6
Toluene C_7H_8 or $C_6H_5.CH_3$
Xylene C_8H_{10} or $C_6H_4(CH_3)_2$
Mesitylene and ψ-cumene C_9H_{12} or $C_6H_3(CH_3)_3$.
Durene $C_{10}H_{14}$ or $C_6H_2(CH_3)_4$.

Propyl-benzene is called cumene, and propyl-toluene is called cymene, the other members being usually named as substitution derivatives of benzene. Their constitution is discussed under BENZENE (*q. v.*).

Occurrence.—In coal-tar, in Galician petroleum, and as hydrides in Caucasian petroleum.

Formation.—1. By distilling their carboxylic acids with lime.—2. By adding strips of sodium to an ethereal solution of a mixture of an aromatic bromide and an alkyl iodide (or bromide) (Fittig's reaction). This reaction takes place the more readily the higher the molecular weight of the alkyl iodide, and where there is already a side chain it succeeds best when this is in the para- position (Krafft a. Göttig, *B.* 21, 3184).—3. By adding $AlCl_3$ to a mixture of an aromatic hydrocarbon with an alkyl chloride, HCl being evolved (Friedel a. Crafts, *A. Ch.* [6] 1, 459; 14, 457; *cf.* ALUMINIUM CHLORIDE, vol. i. p. 147). Friedel a. Crafts consider that this reaction takes place in two stages:

$$C_6H_6 + Al_2Cl_6 = C_6H_5Al_2Cl_5 + HCl$$
$$C_6H_5Al_2Cl_5 + RCl = C_6H_5R + Al_2Cl_6$$

the latter reaction being analogous to

$$ZnEt_2 + 2RCl = 2EtR + ZnCl_2.$$

They have, however, hitherto failed to isolate the hypothetical intermediate body $C_6H_5Al_2Cl_5$, but they have equally failed to obtain the compounds $AlCl_3(C_6H_6)_3$ and $AlBr_3(C_6H_6)_3$ described by Gustavson (*J. R.* 1882, 354), which they regard as mixtures. When MeCl acts on benzene (5 pts.) containing $AlCl_3$ (1 pt.) there is formed s-durene. MeCl acting on toluene in presence of $AlCl_3$ forms *o*-, *m*-, and *p*- xylene, ψ-cumene, mesitylene *s*- and *u*- durene, penta-methyl-benzene, and hexa-methyl-benzene (Ador a. Rilliet, *B.* 12, 329; O. Jacobsen, *B.* 14, 2627). MeCl and $AlCl_3$ converts the three xylenes into ψ-cumene, *m*-xylene giving also mesitylene. The higher homologues of benzene are more readily methylated than the lower. Ethylene passed through a heated mixture of benzene and $AlCl_3$ gives ethyl-, di-ethyl-, and tri-ethyl-benzene (Balsohn, *Bl.* [2] 31, 539). Isomeric changes often occur in these syntheses. Thus isobutyl bromide (300 g.) acting on benzene (900 g.) and $AlCl_3$ (300 g.) at 0° forms *tert*-butyl-benzene (167° at

736 mm.), which is also got from *tert*-butyl chloride; while *n*-butyl chloride gives *sec*-butylbenzene (174° at 735 mm.) (Schramm, *M.* 9, 613). In like manner isoamyl chloride gives an amylbenzene (188° at 737 mm.) which appears to be C_6H_5.CHMePr or C_6H_5.CMe_2Et. *n*-Propyl bromide gives isopropyl derivatives, since PrBr is changed to PrBr in presence of $AlCl_3$ (Kekulé a. Schrötter, *B.* 12, 2280). Schramm supposes the alkyl chloride to be split up into HCl and olefine, the latter then acting like ethylene (*v. supra*). By the action of $AlCl_3$ on boiling toluene there is formed benzene, ethyl-benzene, and the three xylenes (Friedel a. Crafts, *C. R.* 101, 1218). In a similar manner *m*-xylene is converted by $AlCl_3$ into benzene, toluene, mesitylene, and ψ-cumene; while ethyl-benzene gives benzene and di-ethylbenzene (Anschütz a. Immendorff, *B.* 17, 2816; 18, 657). The transference of side chains may be readily effected by passing HCl through the heated mixture of $AlCl_3$ with the hydrocarbon, *e.g.*

$$C_6H_3Me_3 + HCl = C_6H_4Me_2 + MeCl$$
$$C_6H_3Me_3 + MeCl = C_6H_2Me_4 + HCl$$

(Jacobsen, *B.* 18, 343).—4. When aromatic hydrocarbons are heated with MeI or EtI and iodine in sealed tubes at high temperature, Me or Et can be introduced, although very many other products are formed at the same time. In this way benzene heated with MeI gives toluene, toluene (with MeI) gives xylenes, and hydrocarbons C_9H_{12}, $C_{10}H_{14}$, and $C_{11}H_{16}$; while pseudocumene mixed with mesitylene (with EtI) gives $C_6H_3Me_2Et$ (here Et turns out Me) (Rayman a. Preis, *A.* 223, 315).—5. By heating ketones with H_2SO_4; thus acetone gives mesitylene.—6. By heating benzene and its homologues with $ZnCl_2$ and (the higher) fatty alcohols, water being eliminated (Goldschmidt, *B.* 15, 1066).—7. By heating diazo- compounds with alcohol.—8. By boiling hydrazines with $CuSO_4$ or $FeCl_3$.

Reactions.—1. Fuming *nitric acid* dissolves them, and on adding water nitro- derivatives are ppd.—2. Fuming *sulphuric acid* dissolves them, forming sulphonic acids. By distilling the resulting sulphonic acids with superheated steam the hydrocarbons can be recovered, and thus separated from fatty hydrocarbons, and even from one another (Beilstein, *A.* 133, 34; Armstrong a. Miller, *C. J.* 45, 148; Kelbe, *B.* 19, 93). 3. *Halogens* form products by substitution. Heat and direct sunshine both cause the halogen to enter the side chain instead of the benzene nucleus (Schramm, *B.* 19, 212; *M.* 8, 299). Yellow light has the maximum effects. According to Radziszewski (*A.* 218, 386) the halogens acting upon alkyl-benzenes go in the cold into the *p*- position; as the heat is raised they go into the *o*- position, then into the CH_2 attached to the C_6H_5, and at a still higher temperature into the next CH_2, and so on (*v.* Chloro- compounds, and Bromo- compounds).—4. *Chromic acid* mixture oxidises all the side chains to carboxyl, while *nitric acid* (S.G. 1·2) frequently attacks only one side chain. In the oxidation by means of dilute HNO_3 of the di-alkylated benzenes it has usually been assumed that the longest side chain is oxidised first, becoming CO_2H. This is not always the case, for *m*- and *p*-iso-butyl-toluenes give isobutyl-benzoic acids, and the oxidation of all such hydrocarbons is greatly modified by the introduction of halogens into the ring, thus tetra-chloro-*m*-isocymene can only be oxidised with very great difficulty, and then is entirely broken up (Kelbe a. Pfeiffer, *B.* 19, 1723). Propyl-isopropyl-benzene is oxidised to *n*-propyl-benzoic acid.—5. *Chromyl chloride* forms addition compounds $C_nH_{2n-6}(CrO_2Cl_2)_2$. These compounds give off HCl at 200°, becoming $C_nH_{2n-8}(CrO_2Cl)_2$. If they contain methyl they are converted by water into aldehydes. In the case of benzene, water produces quinone (Étard, *A. Ch.* [5] 22, 218; *C. R.* 87, 989).—6. By heating with HIAq the hydrocarbons C_nH_{2n-6} can be made to take up 2, 4, or 6 atoms of hydrogen. The hydrides $C_nH_{2n-6}H_6$ occur in Caucasian petroleum (Beilstein a. Kurbatoff, *B.* 13, 1818) and may also be obtained by the distillation of colophony (Renard, *A. Ch.* [6] 1, 227).

Homologues of Anthracene C_nH_{2n-18} may be formed as follows: 1. From anthranols by abstraction of water (Liebermann a. Tobias, *B.* 14, 795).—2. From halogenated hydrocarbons, by heating under pressure (Dorp, *A.* 169, 210).—3. From halogenated methanes, aromatic hydrocarbons, and $AlCl_3$ (Anschütz a. Romig, *B.* 18, 664; Elbs a. Wittich, *B.* 18, 848).—4. From homologues of diphenylmethane by abstraction of hydrogen (Weiler, *B.* 7, 1185; Fischer, *B.* 7, 1195).—5. From homologues of *o*-tolyl-phenyl ketone by abstraction of water (Behr a. Dorp, *B.* 7, 17; Elbs, *J. pr.* [2] 33, 186).—6. Phthalic anhydride, aromatic hydrocarbons, and $AlCl_3$ give homologues of *o*-benzoyl-benzoic acid, whence by conc. H_2SO_4 homologues of anthraquinone may be obtained. Thus toluyl-benzoic acid [2:1]$C_6H_4(CO_2H)CO.C_6H_4(CH_3)$[1:4] from phthalic anhydride and toluene gives (*B.* 2)-methyl-anthraquinone [175°], while *m*-xyloyl-*o*-benzoic acid gives a dimethyl-anthraquinone [162°] (Elbs, *J. pr.* [2] 33, 318).

Hydrocarbons of the tri-phenyl-methane series C_nH_{2n-22} (Elbs *J. pr.* [2] 33, 181) may be formed as follows: 1. From chloroform or chloropicrin, benzene or homologues of benzene, and $AlCl_3$.—2. From benzylidene chloride, benzene or homologues of benzene, and zinc-dust.—3. From secondary aromatic alcohols, aromatic hydrocarbons, and P_2O_5 (best method).—4. From aromatic (β)-pinacolins and alkalis (Thörner a. Zincke, *B.* 10, 1475; 11, 65).—5. From benzylidene chloride (or its homologues) and $Hg(C_6H_5)_2$ (or its homologues).—6. From benzoic aldehyde, benzene or its homologues, and $ZnCl_2$ at 250°.

HYDROCARBOSTYRIL *v.* *o*-Amido-β-phenyl-propionic acid.

DI-HYDRO-CARBOXYLIC ACID (so-called) *v.* Tetra-oxy-quinone.

Tri-hydro-carboxylic acid (so-called) *v.* Hexa-oxy-benzene.

HYDRO-CAROTINE *v.* Carrotin.

HYDROCHELIDONIC ACID *v.* Chelidonic acid.

HYDRO-CHLORANILIC ACID *v.* Di-chloro-tetra-oxy-benzene.

HYDROCHLORIC ACID *v.* Chlorhydric acid, p. 5.

HYDROCHLOROCARVOL *v.* Carvol chlorohydride.

HYDROCHLOROCINCHONINE *v.* Cinchonine chlorohydride.

HYDROCHLOROCONQUININE *v.* Cinchona bases.

HYDROCINCHONIDINE *v.* Cinchona bases.

HYDROCINCHONINE *v.* Cinchona bases and Cinchonine.

HYDROCINNAMENYL-ACRYLIC ACID *v.* Phenyl-pentenoic acid.

HYDROCINNAMIC ACID *v.* Phenyl-propionic acid.

HYDROCINNAMIDE $C_{27}H_{24}N_2$ *i.e.* $N_2(CH.CH:CHPh)_3$. [106°]. White needles. Formed by the action of NH_3 on an alcoholic or ethereal solution of cinnamic aldehyde. It is very stable towards HCl at a high temperature.

Salts.—B′HCl3aq: flat colourless tables: [220°]; sol. alcohol and chloroform, insol. water, ether, benzene, and ligroïn. — $B'_2H_2Cl_2PtCl_4$ (Laurent, *Rev. Scient.* 10, 119; Peine, *B.* 17, 2110).

HYDROCOLLIDINE *v.* Tri-methyl-pyridine hydride.

HYDROCONQUININE *v.* Cinchona bases.

HYDROCORNICULARIC ACID *v.* Cornicularic acid.

HYDROCOTARNINE *v.* Narcotine.

HYDROCOTOÏN *v.* Coto bark.

HYDROCOTONE *v.* Coto bark.

HYDRO-*p*-COUMARIC ACID *v.* *p*-Oxy-β-phenyl-propionic acid.

HYDROCOUMARILIC ACID *v.* Coumarilic acid.

HYDROCOUMARIN *v.* *Anhydride* of Oxy-phenyl-propionic acid.

HYDROCROCONIC ACID *v.* *Hydride* of Croconic acid.

HYDROCUMINOÏN *v.* Cuminoïn.

HYDRO-ψ-CUMOQUINONE $C_6HMe_3(OH)_2$ [1:2:5:3:6]. [169°]. Formed by reducing ψ-cumoquinone (Nölting a. Baumann, *B.* 18, 1152). Needles (from water); sl. sol. cold, v. sol. hot, water.

HYDROCYANALDINE *v.* vol. i. p. 104.

HYDROCYANIC ACID *v.* Cyanhydric acid, p. 300.

HYDROFERRICYANIDES *v.* Ferricyanides, p. 337.

HYDROFERROCYANIDES *v.* Ferrocyanides, p. 333.

HYDRO-FERULIC ACID *v.* *Methyl derivative* of Di-oxy-phenyl-propionic acid.

HYDROFLUOBORIC ACID *v.* Borofluorhydric acid, vol. i. p. 526.

HYDROFLUORIC ACID *v.* Fluorhydric acid, p. 558.

HYDROFLUOSILICATES *v.* Fluosilicates, under Silicates.

HYDROGALLEÏN *v.* Galleïn.

HYDROGARDENIC ACID *v.* Gardenin.

HYDROGEN H. At. w. 1. Mol. w. 2. S.G. (air = 1) ·06926 (Regnault, at 0° and 760 mm. At sea-level latitude of Paris). Ratio of S.G. of H to that of O = 15·884 (Rayleigh, *N.* 37, 418; 39, 462). S.G. at 3,000 atmos. (water = 1) = ·0887 (Amagat, *C. R.* 107, 522). S.G. liquid at 0° = ·025, at −23° = ·032 (Cailletet a. Hautefeuille, *C. R.* 92, 1086). S.H. 2·411 referred to equal weight of water; ·99 referred to equal volume of air; ratio of S.H.'s at constant pressure and constant volume 1·3852 (Clausius, *Mechan. Wärmetheorie*, 1, 62). C.E. (0° to 100°) ·0036678 (constant volume); ·0036613 (constant pressure) (Regnault, *A. Ch.* [3] 5, 52). S (0° to 20°) ·0193; S. (alcohol at 0°) ·06925 (Bunsen, *Gasomet. Methoden*, 154).

Compressibility-coefficient 1000–1500 atmos. ·000408, 1500–2000 atmos. ·000272, 2000–2500 atmos. ·000197, 2500–3000 atmos. ·000158 (Amagat, *C. R.* 107, 522). On the compressibility of H for temperatures from −183° to +100° and pressures from 1 to 70 atmos. *v.* Wroblewski (*M.* 9, 1067; or *Nature*, 39, 583). H.C.p. $[H^2,O]$ = 68,360 at c. 18°, product liquid H_2O; $[H^2,O] = 57{,}903 + 1{\cdot}6\,t$, elements and product gaseous (Thomsen). Chief lines in emission-spectrum Hα 6562·1, Hβ 4860·7, Hγ 4339·3, Hδ 4101·2 (Angström, *Spectre solaire*, Upsala, 1868).

The recognition of H as an individual gas was made by Cavendish in 1766. The name *hydrogen* was given by Lavoisier.

Occurrence.—In small quantities in the gases from volcanoes and fumaroles (Bunsen, *P.* 83, 167). In the gases issuing from the salt beds at Stassfurt (Reichardt, *Ar. Ph.* [2] 103, 347; Precht, *B.* 13, 2326); and at Wieliczka (H. Rose, *P.* 48, 353). Also condensed in certain meteorites (Graham, *Pr.* 15, 502; Mallet, *Pr.* 20, 365). In the intestines of several animals, produced by decomposition of organic material (Tappeiner, *B.* 14, 2375). Occurs also in the sun and many fixed stars. Compounds of H occur in large quantities; the chief compound is water; H is a constituent of almost all organic matter; compounds of H with Cl, S, and N also occur in fairly large quantities.

Formation.—1. By electrolysis of acidulated water.—2. By the reaction of many metals with H_2O; K, Na, and other alkali metals decompose cold H_2O rapidly, forming hydroxides and H; Zn, Fe, Mg, Al, and many other metals decompose steam, forming oxides and H.—3. By passing steam over hot C, CO_2 is also formed.—4. By heating CaO_2H_2, BaO_2H_2, NaOH, or KOH, with C; $C + CaO + 2H_2O = CaCO_3 + 2H_2$.—5. By the reactions of many metals with dilute solutions of acids, especially of HCl and H_2SO_4; HNO_3 cannot be used, as oxides of N are produced. 6. By heating KOHAq with Zn and Fe, or with Al, or Mg, or certain other metals.—7. By decomposing NH_4 salts (not NH_4NO_2) in solution by Zn; the action proceeds at c. 40° (Lorin, *C. R.* 60, 745).—8. By heating alkali formates or oxalates with KOH.

Preparation.—1. *Pure* granulated zinc is placed in a capacious flask, and a *cold* mixture of about 1 vol. *pure* H_2SO_4 with c. 8 vols. H_2O is added. Addition of a little *pure* $CuSO_4Aq$ prevents evolution of H_2S (by forming CuS) which may be produced even with pure acid and Zn (Löwe, *D. P. J.* 211, 193). The contents of the flask must remain quite cold during the process; if temperature rises, traces of H_2S and SO_2 begin to be evolved. The gas is passed through (1) conc. $KMnO_4Aq$ to remove traces of AsH_3, SbH_3, and PH_3 (Schobig, *J. pr.* [2] 14, 289); (2) a U tube containing pumice soaked in $AgNO_3Aq$ or $HgCl_2Aq$ to remove the last traces of H_2S, AsH_3, &c., the pumice should be first moistened with H_2SO_4 and strongly heated in a crucible, to remove chlorides; (3) a U tube containing pumice or glass beads moistened with conc. KOHAq to remove any acid that may have been carried over from the generating flask; (4) a series of tubes containing (*a*) dry $CaCl_2$ in small lumps, (*b*) dehydrated, white $CuSO_4$, (*c*) a considerable length of P_2O_5. If the H is not required to be dry the last series of tubes will be omitted. If the H is to be used for reducing metallic oxides, &c., Winkler recommends to pass it through a red-hot tube packed with iron-wire gauze rolled together (*B.* 22, 896 *note*).—2. Pure KOHAq is heated with pieces of Al; the gas is passed through the same purifying tubes as 1, omitting the KOH tube.—3. By heating a mixture of HCO_2K and KOH, or $C_2O_4K_2$ and KOH: $2HCO_2K + 2KOH = 2K_2CO_3 + 2H_2$:$C_2O_4K_2 + 2KOH = 2K_2CO_3 + H_2$ (*cf.* Pictet, *A.Ch.* [5] 13, 216).—4. By electrolysing 10 p.c. pure H_2SO_4Aq, the positive electrode being immersed in a mass of liquid Zn-amalgam (*v.* Analysis, vol. i. p. 240).

Properties.—A colourless, tasteless, odourless, gas; liquefied under great pressure and at a very low temperature. Olzewski (*C. R.* 98, 913; 99, 133) liquefied H by surrounding the gas with N boiling *in vacuo*, the temperature of the N was −213°; the liquid H appeared as colourless drops on the sides of the tube. According to Olzewski the critical temperature of H is lower than −198°; Sarrau gives −174·2° as the critical temperature (*C. R.* 94, 639; 718, 845). Wroblewski (*M.* 9, 1067) gives critical temperature −240°; critical pressure 13·3 atmospheres; and critical volume ·00335. If these results are confirmed, they show that Pictet's statement that H is liquefied at −149° is erroneous. Pictet (*C. R.* 86, 106) subjected H at c. −140° to a pressure of 360 atmospheres; on opening the stopcock an opaque steel-blue jet issued; Pictet describes the fall of this jet on the floor as producing a sound like the rattling of shot. Cailletet obtained liquid H by suddenly reducing the pressure on the gas at 300 atmospheres (*A. Ch.* [5] 15, 132).

H is the lightest known substance; 1 litre at 0° and 760 mm. at the latitude of 45° weighs ·08952289 gram (mean of results of Regnault [*Acad.* 21, 158] and Jolly [*W.* 6, 520]). H is about 14½ times lighter than an equal volume of air, 11,160 times lighter than water, 151,700 times lighter than Hg, and 236,000 times lighter than Pt. H is only v. sl. sol. water. It diffuses rapidly through porous membranes, such as porcelain or paper; also through several metals at red heat (Graham, *Pr.* 15, 223; 16, 429; 17, 212, 500).

Large volumes of H are absorbed by Pd and several other metals, especially when the metal is made the negative electrode in the electrolysis of H_2O. Graham (*Pr.* 15, 502; 16, 422) found that Pd foil which had been heated *in vacuo* occluded 376 vols. H at the ordinary temperature, 643 vols. at 90°–97°, and 526 vols. at 245°. A Pd wire used as the negative electrode in electrolysing water occluded 935 vols. H, and increased in length from 609·14 mm. to 618·91 mm. From such data Graham calculated the S.G. of the occluded H to be ·733; later determinations by Dewar gave ·62 (*P. M.* [4] 47, 324). *v. infra* Hydrogenium. According to Troost a. Hautefeuille (*C. R.* 78, 968) Pd and H form a definite compound Pd_2H; they think that this compound is formed when H is occluded by Pd, and the compound then continues to occlude or absorb more H T. a. H. heated the Pd which had occluded H in a closed space in connexion with a manometer, a portion of the H was evolved without establishment of any definite relation between the pressure and temperature, but when the H remaining was in the ratio H:2Pd, a definite relation was established between pressure and temperature, so that for each temperature there was a certain pressure whereat evolution of H ceased, and this pressure was independent of the relative masses of H and Pd. According to Favre (*C. R.* 77, 649; 78, 1257) for each gram of H occluded by Pd, about 9,000 gram-units of heat are produced. T. a. H. found that K and Na also occlude H, 1 vol. of K occluded 126 vols. H at c. 300°, the formula K_2H requires 124·6 vols. H. Na also seems to form a compound Na_2H. Li at 500° and 760 mm. occluded 17 times its volume of H; Tl only 3 times its volume. (For the dissociation-pressures of the compounds Pd_2H, K_2H, and Na_2H *v.* Dissociation, p. 398; for more details as to the properties of these bodies *v.* Palladium, Potassium, Sodium.) Thoma has carefully investigated the absorption of H by metals (*Z. P. C.* 3, 69). He finds that Pd, made the negative electrode during electrolysis of water, takes up and retains a definite quantity of H; but that after this saturation-point is reached the Pd continues to absorb H, which, however, it readily gives up again; the total quantity of H absorbed depends on the strength of the current; when no more is taken up, it is very probable that H continues to be absorbed, but that as much is evolved as is absorbed in a given time; the increase in the volume of the Pd, for a given quantity of H absorbed, is greater when the saturation-point is passed than before it is reached, hence the relative density of what may be called the occluded H in excess is less than that of the H absorbed up to the saturation-point. Thoma has shown that Fe, like Pd, may be supersaturated with H, provided the H is produced in contact with the Fe. Plates or wires of Ni, and also Al, ppd. Cu, Cu wire, Pt black, Pt wire, and Ag wire, absorb H showing phenomena similar to Fe (Thoma, *l.c.*; Raoult, *C. R.* 1869. 826; Bellati a. Lussana, *Atti del R. instituto veneto d. Scienze, lettere ed arti*, 6, 6 [1888]).

H is a reducer; it removes O and most other negative elements from their compounds. Occluded H is a very active reducing agent: KNO_3Aq is reduced to KNO_2Aq (Böttger, *B.* 6, 1396); ferric salts are reduced to ferrous, K_3FeCy_6Aq is reduced to K_4FeCy_6Aq (Graham, *Pr.* 17, 500); $KClO_3Aq$ is reduced to KClAq; H_2SO_3Aq gives H_2S, As_2O_3Aq is reduced to As (Gladstone a. Tribe, *C. J. Trans.* 1878. 308; *cf.* Berliner, *W.* 35, 791; also Cooke, *C. N.* 58, 103).

The atomic weight of H is taken as unity; the relation between the atomic weights of H and O is very important as so many atomic weights are determined in terms of that of O. Various experiments have recently been made to determine the ratio of the densities of H and O directly; if this is known, and the ratio of the combining weights of these elements is also known, the ratio of the atomic weights of H and O will be directly determined. The most accurate determinations (which cannot, however, be regarded as final) give the ratio S.G. of H:S.G.

of O = 1:15·884 (*v.* Rayleigh, *N.* 39, 462). The atom of H is the standard monovalent atom in terms of which the valencies of the other atoms are stated. The S.G. of gases is also generally stated in terms of H.

H is a combustible gas; it may be burnt in O, Cl, I, S vapour, &c.; if O is caused to flow from a narrow orifice into a quantity of H which has been ignited at the opening of the containing vessel, combination occurs at the edges of the moving stream, and hence the O appears to burn, and the H to act as the supporter of combustion. The flame of H is almost non-luminous; the temperature is very high.

Hydrogenium. This name was given by Graham to hydrogen when it is occluded by Pd (*Pr.* 17, 212, 500). The experiments of Graham, Dewar, Troost a. Hautefeuille, and Thoma, have shown that when H is occluded by Pd it is very much condensed (for references *v. supra*). Graham looked on H as a metal, and Pd charged with H he regarded as an alloy, hence to H alloyed with Pd he gave the name *hydrogenium* (names of metals generally end in *um*). There seems little doubt that a certain definite quantity of H is held by Pd in firmer union than the rest of the H which it is able to occlude (*v.* Thoma, *supra*).

Reactions.—1. H is burnt to H_2O by mixing with ½ its volume of *oxygen*, and applying a light or passing an electric spark; the process is explosive. The exact ratio of the volumes of H and O which combine cannot yet be regarded as settled; according to the experiments of Scott (*T.* 184, 543) the most probable value is O:H = 2·002:1 (*cf.* WATER, vol. iv.).—2. H reduces many *metallic oxides*, *sulphides*, and *chlorides*: *e.g.* CuO and Fe_2O_3 heated in H are reduced to Cu and Fe respectively; Sb_2S_3 is reduced to Sb; $FeCl_2$ is reduced to Fe. PdO is reduced at the ordinary temperature (Wöhler, *A.* 174, 60). Regarding the temperatures at which various oxides, sulphides, and chlorides are reduced by H *v.* Müller (*Z.* [2] 5, 507; also Wright a. Luff, *C. J. Trans.* 1878. 1). H also reduces many *metallic salts* in solution; *e.g.* warm solutions of chlorides of Pt, Pd, Ir, or Rh, are reduced with ppn. of the metals; some salts in solution are reduced only under considerable pressure, *e.g.* $HgCl_2Aq$ is reduced at 100 atmos. The reduction of $AgNO_3Aq$ by H proceeds very slowly at ordinary temperature (*v.* Russell, *C. J.* [2] 12, 3). As already stated (*supra*) Pd or Pt charged with H is a very energetic reducing agent. (Regarding the reaction of H and O in presence of CO *v.* CARBON, vol. i. p. 690.)

Combinations.—1. H combines indirectly with *copper* to form Cu_2H_2 (*v.* COPPER HYDRIDE); it probably also combines with *palladium*, *potassium*, and *sodium* (*v. supra*).—2. H combines with all the *non-metals*; directly with C, N, O, S, Se, Te, ?F, Cl, Br, I; indirectly with P, As, Sb, Si, ?B (*v.* the various elements).

Nascent hydrogen.—Certain reductions not brought about by H are effected when a chemical change in which H is produced is carried out in presence of the body to be reduced; *e.g.* $KClO_3Aq$ is not reduced by passing H through the solution, but if Zn and dilute H_2SO_4Aq are placed in the solution KCl is formed; so $C_6H_5NO_2$ is not reduced by H under ordinary conditions, but if Fe filings and dilute acid are brought into contact with $C_6H_5NO_2$ aniline ($C_6H_5NH_2$) is formed. It is customary to speak of such reactions as these as brought about by *nascent hydrogen*. That the reduction of $KClO_3Aq$, for instance, is not to be wholly traced to the H produced in contact with it is proved by the fact that Na-amalgam does not reduce this salt, although H is plentifully produced when Na-amalgam is placed in the solution (Tommasi, *P. B.* 2, 205). Nascent H is generally regarded as synonymous with atomic H, and it is contrasted with ordinary or molecular H. It is probable that H consists for the most part of atoms at the moment of its production from a compound, and that these then combine to form molecules. As energy must be degraded in the falling together of the atoms into molecules we should expect atoms of H to be capable of bringing about chemical changes that could not be accomplished by molecules of H. But the facts cited with regard to the reduction of $KClO_3$, and there are many similar facts, show that—granting that H is produced in atoms when Zn and H_2SO_4Aq, or Na-amalgam and water, react—the whole of the chemical change must be looked to, and attention must not be concentrated only on the H. If we start with the system Zn, H_2SO_4Aq, $KClO_3Aq$, we may pass to the system $ZnSO_4Aq$, H_2, $KClO_3Aq$, or to the system $ZnSO_4Aq$, KClAq, H_2O, or to a system which consists of all these products; more energy is probably degraded in passing to the third system than to any of the others; this system is produced. But this view does not hinder us from saying that when the Zn and H_2SO_4Aq form $ZnSO_4Aq$ and hydrogen, it is atoms of H that are formed, and that some of these combine to form molecules, and others react with the $KClO_3$ to form KCl and H_2O. In the case of Na-amalgam and $KClO_3Aq$ it is probable that much more energy is degraded in passing to the system NaOH, H_2, Hg, $KClO_3$, than to the system NaOH, Hg, KCl, H_2O. Probably also in the case of Zn and H_2SO_4Aq the energy produced suffices to decompose some of the $KClO_3$, and so KCl and H_2O are formed; whereas the energy produced in the reaction of Na-amalgam with H_2O is not (by hypothesis) sufficient to decompose any $KClO_3$.

Chemical relations of hydrogen.—H stands apart from the other elements. In its relations to O, Cl, S, and other negative elements, it plays the part of a metal; in its relations to the paraffins C_nH_{2n+2} and paraffin alcoholic radicles C_nH_{2n+1} it exhibits properties not at all characteristic of metals. H is a constituent of all acids, and also of all alkalis. Some of the binary compounds of H are powerful acids, some are alkalis, some are neutral bodies. In the periodic arrangement of the elements H is placed as the only member of series 1. The difference between the atomic weights of two consecutive members of the same group, in odd and even series, is about 22; the difference between the atomic weight of H and that of Li, which follows H in Group I, is 6.

References to older works on hydrogen.—Scheele, *Crell Ann.* 1785. ii. 229, 291; Cavendish, *Crell Ann.* 1785. i. 324; Watt *Crell Ann.* 1788. i. 23, 36; Meusnier a. Lavoisier, *Crell Ann.* 1788. i. 354, 441, 528; Berzelius a.

Dulong, *A. Ch.* 15, 386; Dumas, *C. R.* 14, 537.

Hydrogen antimonide. Described under ANTIMONY, vol. i. p. 288.

Hydrogen arsenides. Described under ARSENIC, vol. i. p. 310.

Hydrogen boride *v.* BORON HYDRIDE, vol. i. p. 526.

Hydrogen bromide *v.* BROMHYDRIC ACID, vol. i. p. 532.

Hydrogen carbides *v.* HYDROCARBONS, this vol. p. 715.

Hydrogen chloride *v.* CHLORHYDRIC ACID, this vol. p. 5.

Hydrogen fluoride *v.* FLUORHYDRIC ACID, this vol. p. 558.

Hydrogen iodide *v.* IODHYDRIC ACID in vol. iii.

Hydrogen nitride *v.* AMMONIA, vol. i. p. 196.

Hydrogen oxides. Two oxides of hydrogen are known, H_2O and H_2O_2. The former has been gasified, and its molecular composition is represented by the formula H_2O; the latter is decomposed by heat, the gaseous molecule H_2O_2 cannot exist, therefore the formula H_2O_2 represents the composition of the chemically reacting atomic aggregate of this compound. Water is a stable compound; in its chemical relations it is a neutral oxide; its typical reaction with a metal is to produce an oxide and H, its typical reaction with a non-metal is to produce a hydride and O. Hydrogen peroxide readily parts with ½ of its O, and therefore acts generally as an oxidiser. Water combines with many compounds and with some elements to form hydrates, with other compounds and elements it reacts to form hydroxides (*v.* HYDRATES and HYDROXIDES, pp. 703, 733); hydrogen peroxide directly combines with but few other bodies.

HYDROGEN MONOXIDE or WATER, *v.* WATER, in vol. iv.

HYDROGEN DIOXIDE H_2O_2. (*Hydrogen peroxide. Oxygenated water.* Sometimes also called *hydroxyl*, but this term is now almost universally retained for the radicle OH.) This compound was first prepared by Thénard in 1818. (Thénard's chief memoirs are contained in *A. Ch.* 8, 306; 9, 51, 94, 314, 414; 10, 114, 335; 11, 85, 205; 50, 80.) H_2O_2 has not been obtained quite free from water.

Occurrence.—In rain-water and snow (Struve, *Z.* [2] 5, 274; Houzeau, *C. R.* 70, 519; *cf.* ATMOSPHERE, vol. i. p. 333). Acording to Clermont (*C. R.* 80, 1591) H_2O_2 occurs in the juices of tobacco plants, vines, and lettuces; Wurster (*B.* 19, 3195) asserts the occurrence of H_2O_2 in many animal and vegetable secretions; but Bokorny (*B.* 21, 1100) points out that his test was inconclusive.

Formation.—1. By decomposing various peroxides by dilute acids, *e.g.* BaO_2 by H_2SO_4Aq, HClAq, CO_2Aq, or H_2SiF_6Aq, or K_2O_4 by tartaric acid (*v.* Thénard, *l. c.*; Duprey, *J. pr.* 88, 440; Schönbein, *J. pr.* 77, 263; Osann, *C. C.* 1862. 97; C. Hoffmann, *A.* 136, 188).—2. By shaking Zn or Fe powder with water in presence of air (Schönbein, *J. pr.* 105, 219; Hoppe-Seyler, *H.* 2, 25; 10, 36).—3. By the action of hydrogenised Pd on water in presence of O (Traube, *B.* 15, 659, 2434, 2451; 16, 1201).—4. During the electrolysis of fairly conc. H_2SO_4Aq; dilute H_2SO_4 gives little or no H_2O_2. Richarz (*W.* 31, 912) says that 70 p.c. acid is the best concentration to use. Much work has been done on the source of H_2O_2 in the electrolysis of H_2SO_4Aq. Richarz (*l.c.* and *W.* 24, 183) regards the H_2O_2 as a product of the reaction of $H_2S_2O_8$ (formed by electrolysis) and H_2O; when 68 p.c. H_2SO_4Aq is used, the amount of H_2O_2 increases, and then becomes constant, but the $H_2S_2O_8$ goes on increasing, on stopping the current H_2O_2 increases for a time, and $H_2S_2O_8$ notably decreases. In a solution containing H_2SO_4 and $H_2S_2O_8$ the latter slowly disappears, and H_2O_2 is produced. Traube holds that the H_2O_2 is directly produced by the reaction of ordinary (molecular) O with water and nascent H (*l.c.* and *B.* 19, 1111; 20, 3345). The H_2O_2 is always formed at the negative electrode.—5. According to Berthelot (*C. R.* 86, 71) H_2O_2 is formed by shaking ozone with ether, and then adding water.—6. By the oxidation of very dilute NH_3Aq by ozonised O [? $2NH_3Aq + 2O_2 = NH_4NO_2Aq + H_2O_2$] (Carius, *B.* 7, 1481).—7. By placing a solution of pyrogallol under a bell jar (Struve, *W. A. B.* 68 [2nd part], 432).—8. By burning H in air (Struve, *J.* 1870. 199, 209).—9. By shaking various essential oils containing terpenes with water in presence of air (Schönbein, *J. pr.* 99, 11; Radenowitsch, *B.* 6, 1208; Kingzett, *C. J.* [2] 13, 210).—10. During many processes of oxidation in presence of water (*v.* Schönbein, *J. pr.* 89, 14; 98, 257).

Preparation.—By decomposing BaO_2 by dilute acids.—1. Thénard prepared BaO_2 by heating BaO in small pieces to low redness in a stream of O free from CO_2; the BaO was obtained by strongly heating $Ba(NO_3)_2$; the stream of O was maintained for fifteen minutes after O had apparently ceased to be absorbed. (For method of preparing pure BaO_2 *v.* vol. i. p. 443.) The BaO_2 was allowed to cool in O, and then placed in a stoppered bottle. 200 grams H_2O were then mixed with sufficient HCl to neutralise about 15 grams BaO_2H_2; this dilute HClAq was placed in a Pt vessel surrounded by ice, and 12 grams BaO_2, slightly moistened and rubbed to powder in an agate mortar, were added; the Ba was then ppd. by H_2SO_4Aq; 12 grams BaO_2 were again added, and the Ba was again removed; the liquid was filtered, and addition of BaO_2 in two portions, with ppn. by H_2SO_4Aq, was repeated. These processes were repeated until about 100 grams BaO_2 had been used. SiO_2, Al_2O_3, Fe_2O_3, &c., were removed by adding conc. H_3PO_4Aq and excess of BaO_2. After rapid filtration traces of HCl were separated by cautious addition of powdered Ag_2SO_4 to the liquid surrounded by ice. After another rapid filtration, H_2SO_4Aq was removed by addition either of BaO_2H_2 suspended in water, or of ppd. $BaCO_3$.

2. Pelouze (*v. Berzelius' Lehrbuch*, 1, 411) decomposed BaO_2 by H_2SiF_6Aq, the liquid being kept cold, and filtered from $BaSiF_6$.

3. Thomsen (*B.* 7, 73) dissolves finely-powdered BaO_2 in dilute HClAq until the acid is nearly neutralised; after filtration the liquid is cooled, and BaOAq is added sufficient to ppt. SiO_2, Al_2O_3, and other oxides, and to produce a slight pp. of $BaO_2.8H_2O$; the liquid is again filtered and mixed with conc. BaOAq, whereby crystalline $BaO_2.8H_2O$ is ppd.; this moist pp. may be kept unchanged in a stoppered bottle. Thomsen decomposes the moist $BaO_2.8H_2O$ by

adding it to cold dilute H_2SO_4Aq (not more conc. than 1 part by weight H_2SO_4 to 5 parts H_2O) with constant stirring, until the acid is nearly neutralised; after settling and filtering, he ppts. the remaining acid by cautious addition of dilute BaOAq.

4. Mann (*Chemiker Zeitung*, 12, 857) recommends to add a ¼ p.c. H_3PO_4Aq to commercial H_2O_2, and then, while stirring vigorously, to add BaO_2H_2 until exactly neutral to litmus; then to pour the clear liquid into cold conc. BaOAq, to wash the ppd. $BaO_2.8H_2O$, and to decompose it by dropping into cold dilute H_2SO_4Aq containing 12 p.c. H_2SO_4, removing any excess of acid by dilute BaOAq (*v.* also Schöne, *A.* 192, 257).

The solution of H_2O_2 obtained by one or other of these methods is concentrated *in vacuo* over H_2SO_4, with agitation from time to time; if SiO_2 separates it must be removed, else it will decompose some of the H_2O_2. The liquid begins to give off O when it is so conc. that one volume of it will yield about 250 vols. O, a drop or two of H_2SO_4 is then added, and evaporation is continued. Nearly pure H_2O_2 is thus obtained. 1 vol. will give 475 vols. O. It is kept in stoppered glass tubes surrounded by ice (Thénard). Hanriott (*C. R.* 100, 172) concentrates H_2O_2Aq by distillation under reduced pressure; a solution, 1 vol. of which will give 267 vols. O, can thus be obtained. A solution so conc. that 1 vol. yields c. 70 vols. O is obtained by freezing dilute H_2O_2Aq, crystals of pure H_2O separate (Hanriott, *C. R.* 100, 57).

Properties.—The most conc. solution of H_2O_2 obtained as described under *Preparation* is a syrupy liquid S.G. = 1·453; it does not freeze at −30°; *in vacuo* it volatilises unchanged (Thénard). Has a harsh bitter taste; corrodes the cuticle. Thomsen gives the thermal data: $[H^2,O^2,Aq] = 45,300$; $[H^2O,O,Aq] = -23,060$; $[H^2O^2Aq,H^2] = 91,420$ (*Th.* 2, 59); Berthelot gives $[H^2O^2 = H^2O + O] = 21,480$ (*A. Ch.* [5] 6, 209). According to Hanriott (*Bl.* [2] 43, 468) conc. H_2O_2Aq has an acid reaction towards turmeric, and an odour resembling that of nitric acid. H_2O_2Aq slowly decomposes; if very dilute it may be kept indefinitely (Berthelot, *C. R.* 90, 897); very dilute solutions may even be boiled without change (Hanriott, *C. R.* 100, 57). Traces of impurities greatly modify the stability of H_2O_2Aq; acids increase, alkalis decrease, the stability. Very conc. H_2O_2Aq rapidly evolves O at 20°; heated quickly to 100° O is evolved with explosion; 1 vol. of the most conc. solution obtained by Thénard gave 475 vols. O at 0° and 760 mm. It is customary to state the conc. of commercial H_2O_2Aq as so many volumes, *e.g.* '20 volumes;' this means that 20 volumes O are obtainable from 1 vol. of the solution. H_2O_2 is soluble in all proportions in water, also in alcohol; but it slowly reacts with the alcohol; sl. sol. ether. On shaking this solution with water the H_2O_2 all goes into solution in the water (Schönbein, *J. pr.* 78, 92). An acidified solution of H_2O_2 is decomposed to H and O by electrolysis. According to Schöne (*A.* 197, 137), the H_2O_2 does not undergo electrolysis, but is decomposed by reacting with the products of electrolysis of the dilute acid present, probably (i.) $H_2O_2 + O = H_2O + O_2$, (ii.) $SO_4 + H_2O_2 = H_2SO_4 + O_2$, (iii.) $H_2 + H_2O_2 = 2H_2O$.

Reactions.—H_2O_2 contains a larger percentage of O (94·1 p.c.) than any other compound; it readily parts with ½ of its O, and therefore reacts as an oxidiser; in some cases, however, it acts as a reducer, *e.g.* Ag_2O is reduced to Ag and PbO_2 to PbO (*v. infra*).

1. *Aluminium*, *iron*, *magnesium*, and *thallium* are oxidised to the hydrates FeO_3H_3, AlO_3H_3, MgO_2H_2 and TlO_3H_3, according to Weltzien (*A.* 138, 129).—2. Most *metals* except Au and the Pt metals are changed to oxides. 3. Several *non-metals* are oxidised, generally to their highest oxides, *e.g.* Se and As.—4. Very many *oxides* and *oxyacids* are converted into more oxidised compounds, *e.g.* As_2O_3 to As_2O_5, H_3PO_3 to H_3PO_4, CaO, SrO, and BaO to the dioxides MO_2, ferrous to ferric compounds, PbS to $PbSO_4$, Tl_2O to Tl_2O_3 (*v.* Schöne, *A.* 196, 98), K_4FeCy_6 to K_3FeCy_6 (Weltzien, *A.* 138, 129). Several *metallic salts* yield peroxides when treated with H_2O_2 in presence of ammonia, *e.g.* salts of Bi, Ce, Co, Ni.—5. *Sulphuretted hydrogen* very slowly forms H_2O and S (Fairley, *C. J.* [2] 16, 23).—6. *Hydrogen iodide* forms H_2O and I.—7. A solution of *chromic hydrate in potash* is oxidised by H_2O_2 to K_2CrO_4 (*cf. Reaction* 11 *infra*).—8. *Ammonia* in solution is oxidised to NH_4NO_2 $[4NH_3Aq + 6H_2O_2 = 2NH_4NO_2Aq + 8H_2O]$ (Weith a. Weber, *B.* 7, 1745).—9. According to Fairley (*C. J.* [2] 16, 125) the unstable compound $Na_2O_2.8H_2O$ is formed by adding alcohol to a mixture of equivalent weights of H_2O_2 and *caustic soda* (*v.* also Schöne, *A.* 192, 241). *Caustic potash* reacts somewhat differently, giving a mixture of K_2O_4 with $KOH.xH_2O$ (Schöne, *l.c.*).

10. H_2O_2 *reduces ozone*, forming H_2O and oxygen. Brodie (*T.* 1850. 759) showed that ½ of the O comes from the ozone and ½ from the H_2O_2; this result was confirmed by Schöne (*A.* 196, 239); Schöne used neutral solutions of H_2O_2, Brodie used alkaline solutions.—11. Several *metallic peroxides* are *reduced* by H_2O_2 in presence of acid. For instance CrO_3 in H_2SO_4 solution gives a blue colour, but this soon goes, and green Cr_23SO_4 is produced (*cf. Reaction* 7 *supra*); Berthelot thinks that perchromic acid $HCrO_4$ is formed and then reduced by the excess of H_2O_2; Moissan regards the blue body as $CrO_3.H_2O_2$ (*v.* CrO_3 under CHROMIUM, p. 166); MnO_2 in presence of an acid forms a salt of MnO and evolves O; for every MnO_2 used, O_2 is evolved (*cf. Reaction* 19 *infra*). Brodie showed that in such cases ½ of the O evolved comes from the H_2O_2 and ½ from the metallic peroxide (*C. J.* 4, 194; 7, 304; *cf.* Aschoff, *J. pr.* 81, 401). According to Lenssen (*J. pr.* 81, 278) H_2O_2 oxidises metallic oxides in presence of alkalis when the alkali can combine with the higher oxide produced by the H_2O_2, to form a salt—*e.g.* Cr_2O_3 to CrO_3 in presence of KOH—but it reduces higher to lower oxides in presence of acids when the acid forms a stable salt with the lower oxide, *e.g.* CrO_3 to Cr_2O_3 in presence of H_2SO_4. 12. *Potassium dichromate* is *reduced* by H_2O_2 in neutral solutions to CrO_2, in acid solutions to a salt of Cr_2O_3 (Schönbein, *J. pr.* 70, 257; Aschoff, *J. pr.* 81, 401).—13. *Potassium permanganate* in presence of H_2SO_4 is *reduced* to $MnSO_4$, thus $2KMnO_4Aq + 3H_2SO_4 + 5H_2O_2 = K_2SO_4Aq + 2MnSO_4Aq + 8H_2O + 5O_2$. In this case also ½ the O comes from the H_2O_2 and ½

from the $KMnO_4$. According to P. Thénard (*C. R.* 75, 177) H_2O_2 and $KMnO_4Aq$ react when kept at a low temperature, but no O is evolved; Berthelot (*C. R.* 90, 656) confirms this, he thinks an oxide $H_2O_2.xO$ is formed.—14. *Silver oxide*, Ag_2O, is *reduced* to Ag by H_2O_2; $Ag_2O + H_2O_2 = H_2O + O_2 + 2Ag$: HgO reacts similarly. Berthelot (*C. R.* 90, 572) thinks that an oxide Ag_4O_3 is produced.—15. According to Hanriott (*Bl.* [2] 43, 468) H_2O_2 *reduces Fehling's solution.*

16. H_2O_2 reacts with *chlorine* to form HCl and O; $H_2O_2 + Cl_2 = 2HCl + O_2$. Schöne (*A.* 196, 254) thinks the reactions may be $H_2O_2 + OH_2 + Cl_2 = H_2O + O_2 + 2HCl$.—17. *Iodine* forms HI and O, by reacting with dilute H_2O_2Aq; but HI decomposes more conc. H_2O_2Aq to form H_2O and I. In the reaction between I and H_2O_2, an oxyacid of I may be produced and then decomposed; when I is added to KOHAq containing H_2O_2, only KI is formed (no KIO_3) and O is evolved (*cf.* Fairley, *C. J.* [2] 16, 22).

H_2O_2 is decomposed to H_2O and O by several substances which at the close of the reaction remain the same as they were at the beginning.

18. *Platinum, gold, silver*, and *charcoal*, added to H_2O_2, cause evolution of O and formation of H_2O. *Fibrin* and some other organic substances bring about the same change. 19. *Manganese dioxide* added to H_2O_2 produces O and H_2O, and the same quantity of MnO_2 remains as was originally added (for action when an acid is present *v. Reaction* 11 *supra*). 20. *Potassium iodide* with *pure* H_2O_2Aq causes evolution of O, but no I is liberated (Kingzett, *C. J.* 37, 805; Schöne, *A.* 195, 228). Schöne supposes that a series of changes occurs, possibly the K salt of an oxyacid (? hypoiodite) is formed and then reacts with more H_2O_2 to give KI, H_2O, and O. Ordinary commercial H_2O_2Aq liberates I from KI.—21. *Potassium bromide* and *chloride* both cause evolution of O; KBr more slowly than KI, and KCl more slowly than KBr; no Br or Cl is liberated (Schöne, *l.c.*). 22. Certain salts, *e.g.* Na_2SO_4, also decompose H_2O_2, but the salt is the same at the close as at the beginning of the reaction (*v.* Schöne, *l.c.*).

23. The *caustic alkalis* decompose H_2O_2 with formation of O and H_2O; Schöne has examined these reactions; he thinks that the first products are H_2O and compounds $M_2H_4O_6$ (M = alkali metal), these compounds have been isolated (*v. Combinations, infra*); these compounds then decompose to alkali, H_2O, and O. Schöne shows that the rate at which H_2O_2 is decomposed by alkalis is modified by temperature, light, concentration, traces of impurities, and the condition of the surfaces of the containing vessels.

H_2O_2 is a representative peroxide; its reactions are similar to those of BaO_2, SrO_2, &c., and the organic peroxides such as acetyl peroxide $(C_2H_3O)_2O_2$; it cannot be said to have distinctly basic or acidic properties, but on the whole it is more acidic than basic, *e.g.* in the reaction $BaO_2H_2.8H_2O + H_2O_2 = BaO_2.8H_2O + 2H_2O$ there is probably an exchange of the H of H_2O_2 for the metal Ba.

Combinations.—Schöne (*A.* 192, 257) has obtained bodies which are probably compounds of H_2O_2 with the peroxides of the alkali and alkaline earth metals. When 1 equiv. KOH in solution was added to about 3 equiv. H_2O_2, the liquid was evaporated *in vacuo* and the residue dried at −10°, a white solid $K_2O_2.2H_2O_2$ ($= K_2H_4O_6$) was obtained. Using about the same proportions of NaOH and H_2O_2, the compound $Na_2H_4O_6.4H_2O$ ($? = Na_2O_2.2H_2O_2.4H_2O$) was obtained. Both these compounds are easily decomposed by warming with evolution of O. The compound $BaO_2.H_2O_2$ was obtained by direct addition of its constituents, or by adding a certain quantity of NH_3Aq to a Ba salt solution in presence of H_2O_2; this compound is very unstable, it easily goes to BaO_2, H_2O, and O; if the decomposition is effected by warming under water, crystals of $BaO_2.8H_2O$ are formed. Indications of the existence of compounds of H_2O_2 with CaO_2 and SrO_2 were obtained, but the compounds could not be isolated on account of their great instability.

Detection and Estimation.—H_2O_2Aq produces a blue colour in a dilute solution of guaiacum mixed with an infusion of malt. Addition of a few drops of Pb acetate solution, followed by KIAq and starch and a little acetic acid, produces a blue colour (Schönbein, *J. pr.* 86, 129; Struve, *Z.* 1869. 274). Richarz (*W.* 31, 912) says the best reagent for detecting H_2O_2, especially in presence of S_2O_7, is a solution of titanic acid in H_2SO_4; a very yellow pp. is obtained; this pp. decolourises the same quantity of $KMnO_4Aq$ as the H_2O_2 in the solution from which the pp. was obtained (*cf.* Schönn, *Fr.* 9, 41, 330; *D. P. J.* 210, 317).

According to Hanriott (*Bl.* [2] 43, 468) H_2O_2 is best estimated by measuring the amount of O liberated by reacting with MnO_2. It may also be estimated by measuring the quantity of $KMnO_4$ reduced, or the O liberated by reacting with $KMnO_4Aq$; Kingzett (*C. J.* 37, 806) says no acid should be present: the reaction is

$$2KMnO_4Aq + 3H_2SO_4 + 5H_2O_2 = K_2SO_4Aq + 2MnSO_4Aq + 8H_2O + 5O_2.$$

KIAq may be brought into contact with H_2O_2Aq, and the I estimated by dilute standard $Na_2S_2O_3Aq$; best in presence of much dilute H_2SO_4Aq (Kingzett, *l.c.*; *cf.* Schöne, *B.* 7, 1696; Hamel, *C. R.* 76, 1023).

Hydrogen phosphides *v.* PHOSPHORUS, HYDRIDES OF.

Hydrogen selenide H_2Se. (*Selenietted* or *seleniuretted hydrogen. Selenhydric acid. Hydroselenic acid. Selenion hydride.*) Mol. w. 80·8. This compound is the Se analogue of SH_2.

Formation.—1. By leading H over Se heated to c. 400°–500° (Corenwinder, *A. Ch.* [3] 34, 77; Wöhler a. Uelsmann, *A.* 116, 122); or by heating H and Se in a closed tube to c. 440° (Hautefeuille, *C. R.* 64, 608). According to Ditte (*C. R.* 74, 980) combination of H and Se begins at c. 250°, is at its maximum at c. 520°, and then decreases to 750°, where it ceases.—2. By the action of Se on HI gas at the ordinary temperature (Hautefeuille, *Bl.* [2] 7, 198); in presence of water, however, SeH_2 and I give Se and HI. According to Hautefeuille (*C. R.* 68, 1554) SeH_2 and I are produced by heating Se with fairly conc. HIAq in a sealed tube, but on cooling Se crystallises and HIAq remains.—3. By the action of water on Se phosphide ($P_2Se_5 + 6H_2OAq = 2HPO_3Aq + 5H_2Se$). Berzelius recommends this as the best method for preparing H_2Se (*Lehrbuch* [5th ed.], 2, 211).—4. By treating FeSe (obtained by strongly heating Fe with Se) with fairly diluted HClAq (*v.* Divers a. Shimidzu, *C. J.* 47, 441).

Properties.—A colourless gas with most irritating odour, resembling that of SH_2 and Cl combined. Extremely poisonous. A minute quantity of the gas inhaled removes the sense of smell for a time, and produces violent headache. In working with this compound great precautions must be taken. Berzelius thus describes the effect of allowing a bubble of the gas to pass into his nostrils: 'Bei meinem ersten Versuche, den Geruch dieses Gases kennen zu lernen, hatte ich, als eine Gasblase, vielleicht nicht grösser als eine Erbse, in eines der Nasenlöcher gelangt war, für mehrere Stunden so gänzlich den Geruch verloren, dass ich ohne das geringste Gefühl das stärkste Ammoniak unter die Nase halten konnte. Der Geruch kam nach fünf bis sechs Stunden wieder, aber ein sehr heftiger und beschwerlicher Schnupfen hielt vierzehn Tage lang an' (*Lehrbuch* [5th ed.], 2, 213). SeH_2 is more soluble in water than SH_2; the solution reddens litmus; it quickly decomposes in air with ppn. of Se.

Reactions.—1. *Heat* decomposes SeH_2 into Se and H. Ditte (*C. R.* 74, 980) says that the change begins at 150°, is considerable at 270°, but then decreases until it reaches a minimum at 520°, after which it again increases; if H is passed over Se heated to c. 500° SeH_2 is formed, but is again decomposed on coming into the colder part of the tube, so that crystals of Se are formed on those parts of the tube. Ditte's results would show that the dissociation-pressure of SeH_2 does not increase regularly with increase of temperature (*v.* remarks on the action of heat on SeH_2 under DISSOCIATION, p. 398).—2. *Moist air* causes decomposition of SeH_2 with separation of Se.—3. *Electric sparks* cause separation into Se and H (Berthelot, *Bl.* [2] 26, 101).—4. Many *metals* decompose SeH_2 when heated in it; by heating with Sn a volume of SeH_2 gives its own volume of H.—5. Towards *metallic oxides and salts* SeH_2 acts very similarly to SH_2; it ppts. selenides from solutions of many salts.—6. Dilute *sulphurous acid* reacts with excess of H_2Se to form Se and a little SH_2; the reactions probably are (1) $2SeH_2 + H_2SO_3Aq = 2Se + S + 3H_2OAq$, (2) $SeH_2Aq + S = SH_2Aq + Se$ (Divers a. Shimidzu, *C. J.* 47, 441). When H_2Se gas is passed into SO_2Aq a pp. is formed containing both S and Se, probably a selenothionic acid (D. a. S., *l.c.*).—7. When H_2Se is brought into contact with *sulphur* H_2S and Se are at once produced (D. a. S., *l.c.*).

Hydrogen silicide SiH_4 *v.* SILICON HYDRIDE in vol. iv.

Hydrogen, sulphides of. Two sulphides of H are known, H_2S corresponding with H_2O, and a persulphide $H_2S.xS$ probably corresponding with H_2O_2. The sulphide H_2S in solution acts as a weak acid; the persulphide is generally analogous in its reactions to H_2O_2.

HYDROGEN SULPHIDE H_2S. (*Hydrogen monosulphide. Sulphuretted hydrogen. Sulphydric acid. Hydrosulphuric acid. Hydrothionic acid.*) Mol. w. 33·98. [c. −85·5°] (Faraday, *T.* 1845. 1, 155). (c. −61·8° at 760 mm.) (Regnault, *Acad.* 26, 658). V.D. 34. S.G. liquid c. ·9. S.H.p. ·2423 (Croullebois, *A. Ch.* [4] 20, 136). S. at 5° 3·96, at 15° 3·23, at 20° 2·9, at 25° 2·6, at 30° 2·33, at 40° 1·86 (Schönfield, *A.* 93, 26; 95, 10). S. in alcohol at 5° 14·78, at 15° 9·54, at 20° 7·41, at 25° 5·62 (Carius, *A.* 94, 140). H.F. (from white amorphous S) $[H^2,S] = 4,740$; $[H^2,S,Aq] = 9,200$; $[H^2S,Aq] = 4,560$ (*Th.* 2, 63). Vapour-pressures of condensed H_2S in atmos. (Faraday, *T.* 1845. 1, 55) −70° = 1·09, −50° = 2·0, −40° = 2·86, −31° = 3·95, −18·9° = 5·96, −3·33° = 6·36, +8·9° = 13·7, 11·1° = 14·6.

The gas was known in the 16th and 17th centuries; it was first accurately examined by Scheele, who regarded it as a compound of sulphur, phlogiston, and heat.

Occurrence.—In gases from volcanoes and fumaroles. In many mineral waters, *e.g.* the Harrogate water. Sometimes in small quantities in sea-water. It is said to be found in some new wines, probably formed by the acids decomposing sulphides produced by the reduction of sulphates during fermentation.

Formation.—1. By the decay of organic matter containing S compounds, or of organic matter free from S in presence of gypsum.—2. By heating various organic bodies, *e.g.* suet or paraffin (Reinsh, *J. pr.* 1838. 42; Galletly, *C. N.* 24, 162) with S.—3. By the dry distillation of S-containing organic material, *e.g.* gas-coal.—4. By reactions between various acids and metallic sulphides.—5. By the reaction of conc. hot H_2SO_4 with Zn and some other metals.—6. By the electrolysis of conc. H_2SO_4.—7. By heating S with very conc. HIAq.—8. The direct union of H and S occurs when H and S vapour are passed over pumice at c. 400° (Corenwinder, *A. Ch.* [3] 34, 77), or when H is passed over boiling S or is burnt in S vapour (Cossa, *B.* 1, 117; Merz a. Weith, *B.* 2, 341; *cf.* Myers, *B.* 5, 259), or by passing electric sparks through a mixture of H and S vapour (Chevrier, *C. R.* 69, 136; *cf.* Boillot, *C. R.* 70, 97; and also Grove, *C. J.* [2] 1, 263).—9. Boiling water is said not to be decomposed by S (J. de Girard, *C. R.* 56, 797; Gelis, *C. R.* 56, 1014; Geitner, *A.* 129, 351; Cossa, *B.* 1, 111), but the experiments of Cross a. Higgins (*C. J.* 35, 249) make it very probable that when S is boiled with water small quantities of H_2S are produced. By heating H_2O with S to 200° (Geitner, *A.* 129, 351), or by passing steam and S vapour through a glowing glass tube (Myers, *J. pr.* 108, 123) H_2S is produced.

Preparation.—1. Iron sulphide, FeS, in small pieces is placed in a flask connected with a washing apparatus containing water, and dilute H_2SO_4Aq, or HClAq, about 3 to 4 parts water to 1 part conc. acid, is added little by little, with shaking. (The FeS may be conveniently prepared by heating three parts Fe filings with 2 parts powdered S.) If the H_2S is to be collected over water, hot water should be used; if it is necessary to store it in a gasholder a solution of brine should be employed in the gasholder. The gas may be dried by passing through a succession of $CaCl_2$ tubes (H_2SO_4 must not be used, as it decomposes H_2S). The H_2S thus prepared usually contains H (as the FeS usually contains Fe), and frequently hydrides of As and Sb. Various methods have been suggested to get rid of possible traces of AsH_3; O. von der Pfordten recommends to pass the dried gas through a tube containing commercial 'liver of sulphur' heated to 350°-360°, and then through Na_2CO_3Aq (*B.* 17, 2897). Jacobsen (*B.* 20, 1999) says that every trace of As may be removed by passing the gas through 2 or 3 grams of coarsely-powdered, air-dried I, interspersed with glass-wool, placed in a tube at the ordinary temperature.—2. Pure *Stibnite* Sb_2S_3 is decomposed by dilute HClAq; the H_2S is nearly pure.—3. Fresenius (*Fr.* 26, 339) recommends the use of calcium sulphide. It is prepared by strongly heating a mixture of plaster of Paris and charcoal; the sulphide is mixed with one-fourth its weight of plaster of Paris and enough water to make a cream; the whole is poured into shallow paper trays; after setting the block is cut into pieces, which are dried at a gentle heat. By placing the dried pieces in a Kipp's apparatus and adding dilute HClAq, a stream of H_2S is obtained which can be readily controlled.—4. According to Divers a. Shimidzu (*C. J.* 45, 699) an aqueous solution of Mg hydrosulphide is a most convenient source of H_2S, as the pure gas is evolved by heating this solution to c. 60°. The solution is prepared by passing H_2S (made from ordinary FeS) into a large flask about half full of water containing magnesia (preferably freshly calcined) in suspension; not more than about 1 part commercial magnesia should be used to 10 parts water; when the magnesia has all dissolved the solution is placed in a flask with delivery tube and warmed to c. 60° on a water-bath, when a steady evolution of pure H_2S proceeds; by raising the temperature to 90°-100° more H_2S is obtained. The solution of Mg hydrosulphide may be kept unchanged by closing the flask with a cork covered with paraffin. When the solution has been exhausted it is allowed to cool, and then again charged with H_2S, when it is ready for use again.

Many pieces of apparatus have been introduced for the preparation and use of H_2S in laboratories; they are described in *Manuals of Analytical Chemistry.*

Properties.—H_2S is a colourless gas with a most offensive odour; it is very poisonous; sol. in c. ⅓ vol. of H_2O, more sol. in alcohol (*v.* data at beginning of art.). H_2S is liquefied by pressure and cold. The most convenient method, on the small scale, is to place some H persulphide (not thoroughly dried) (*v.* p. 727) in a Λ shaped tube; the persulphide is gradually decomposed by the moisture into H_2S and S; after a few weeks the other limb of the tube is placed in a freezing mixture, and H_2S distils into, and liquefies in, this limb. Melsens (*C. R.* 77, 781) allows charcoal to absorb H_2S, places the charcoal in one limb of a Λ tube, the other limb being in a freezing mixture, and distils. If H_2S made in the ordinary way is to be liquefied by pressure, care must be taken that the gas is free from H. Liquid H_2S is a very mobile, transparent, refractive liquid; S.G. c. ·9; boils at −61·8° at 760 mm. pressure, and solidifies at −85·5°. H_2S is easily burnt in air to H_2O and SO_2; it is decomposed by passing through a hot tube at c. 400° (Myers, *A.* 159, 124), or by passing electric sparks through it. H_2SAq decomposes by exposure to air with separation of S. For an examination of the rate of decomposition of H_2SAq under different conditions *v.* Raab (*N. R. P.* 19, 10). The solution keeps best in a corked bottle inverted under water. In its chemical relations H_2S is similar to H_2O, but it is more decidedly acidic; H_2SAq reacts as a monobasic acid.

Reactions.—1. H_2S is easily decomposed; when *heated* to c. 400° it is separated into its elements (Myers, *A.* 159, 124); it is also decomposed by *electric sparks.* —2. When *burnt in air* SO_2 and H_2O are produced.—3. H_2SAq soon decomposes, with separation of S, by *exposure to the air.*—4. Moist H_2S *warmed in presence of air or oxygen* produces H_2SO_4.—5. Most *oxidising agents* react with H_2SAq to form H_2O, S, and SO_2Aq or SO_3Aq; thus HNO_2Aq and HNO_3Aq produce H_2O, S, and NO; HOClAq produces H_2O, HCl, and S; alkaline iodates are reduced to iodides.—6. *Ferric salts* are reduced to ferrous salts, with separation of S.—7. When H_2S is passed into SO_2Aq until the latter is completely decomposed the solution is known as *Wackenroder's solution*; this liquid probably contains S in suspension, a colloidal form of S in solution, H_2SO_4, $H_2S_3O_6$, $H_2S_4O_6$, $H_2S_5O_6$, and a higher thionic acid, probably $H_2S_6O_6$; if the passage of H_2S is continued until all chemical change ceases the final products are S and H_2O, thus $2H_2S + SO_2 = 3S + 2H_2O$ (Debus, *C. J.* 53, 282; *v.* THIONIC ACIDS, in vol. iv.).—8. H_2S or H_2SAq is decomposed by *chlorine* and *bromine* to HX and S; H_2SAq is similarly decomposed by *iodine*, but if water is not present H_2S does not react with I.—9. Very many *metals* decompose H_2S when heated with it, forming sulphides and H; several metals, *e.g.* Ag, Cu, Hg, react at ordinary temperatures. The decomposition of H_2S by hot Sn or Pt has been employed in the analysis of the compound; a specified volume of the gas is thus found to give its own volume of H.—10. Many *metallic oxides and salts* react with H_2S to form sulphides, and water or acids. The metallic sulphide, if insoluble in, and unacted on by, the acid produced in the reaction, is ppd. when H_2S is passed into a solution of the metallic salt; if the metallic sulphide is decomposed by the acid produced in the reaction, or if it cannot exist in presence of water, no pp. is formed. These reactions are applied in the systematic qualitative analysis of metallic salts (*v.* ANALYSIS, vol. i. p. 220).

11. H_2SAq reacts as a weak monobasic acid, *e.g.* with KOHAq it forms KSHAq. Thomsen (*Th.* 1, 262) gives the following heats of neutralisation:

$$[2NaOHAq,2H^2SAq] = 15,476;$$
$$[4NaOHAq,2H^2SAq] = 15,604;$$
$$[BaO^2H^2Aq,2H^2SAq] = 15,748;$$
$$[2NH^3Aq,2H^2SAq] = 12,390.$$

Combinations.—By compressing H_2S in presence of a little water De Forcrand a. Villard obtained a solid hydrate $H_2S.7H_2O$ (*C. R.* 106, 1402; *cf.* 106, 849 a. 939); this hydrate is easily decomposed by heat. The formation of the hydrate occurs with a large absorption of H_2S gas by the water; when formed at 0°, the pressure being about 60 mm. above the ordinary, 1 c.c. water absorbed about 100 c.c. H_2S, whereas the solubility of H_2S in water at 0° and ordinary pressure is only about 4 vols. in 1 vol. water. Wöhler (*A.* 33, 125) obtained ice-like crystals by leading H_2S into alcohol containing water at −18°, the quantity of water being such that no ice was formed at the temperature of experiment; these crystals may have been a solid hydrate of H_2S.

Detection and estimation.—H_2S is detected by its smell, by its reaction with a salt of Pb or Ag in solution to give brown-black PbS or black Ag_2S, and by the production of a deep purple-red colour when brought into contact with an alkaline solution of Na nitroprusside ($FeCy_5(NO)Na_2$). Finely divided Ag shaken with water containing H_2S forms Ag_2S; it does not, however, decompose alkaline sulphides; these reactions may be applied to detect alkaline sulphides in presence of H_2S; air must not be present, else salts of S oxyacids may be formed. H_2S in aqueous solution may be determined by adding a standardised solution of I in KIAq until a permanent blue colour is produced in presence of starch. The solution of H_2S must be so dilute that not more than ·04 p.c. H_2S is present.

HYDROGEN PERSULPHIDE ?H_2S_2 or H_2S_5. When an acid is added to an aqueous solution of an alkaline or alkaline earth persulphide, H_2S is evolved and the rest of the S is ppd. But if the alkaline persulphide solution is poured into the acid, oily drops sink to the bottom; the oil is a compound of H and S containing relatively more S than H_2S (Schœk, *Von der Luft und dem Feuer*, 153; Berzelius, *Lehrbuch*, 2, 218; Thénard, *A. Ch.* 48, 79; Liebig, *A.* 2, 27; 18, 170). Analyses of the oil thus obtained have given discordant results; Ramsay's analyses (*C. J.* [2] 12, 857) showed a composition varying from H_2S_7 to H_2S_{10}. According to Sabatier (*C. R.* 100, 1346), if the oil is thoroughly dried, it may be distilled at 60°–85° under a pressure of 40 to 100 mm.; and the liquid thus obtained has the composition H_2S_5. The analyses of Rebs (*A.* 246, 356) also point to this formula: he decomposed Na_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5, separately with cold HClAq, also different polysulphides of Ca and Ba; in each case he got an oil the composition of which agreed with the formula H_2S_5. Sabatier thinks that the liquid obtained by him contained S produced by the decomposition of part of the persulphide; he is in favour of the formula H_2S_2 for the persulphide.

Hofmann (*B.* 1, 81) by the reaction between yellow NH_4 sulphide and strychnine obtained a well-crystallised compound $C_{21}H_{22}N_2O_2.H_2S_3$ which was decomposed by acids with separation of H persulphide; this formula was confirmed by Ramsay (*C. J.* [2] 12, 857). Schmidt allowed H_2S to react with strychnine in presence of air, and obtained crystals of $3C_{21}H_{22}N_2O_2 2H_2S_2$; with brucine he got the compounds $C_{23}H_{26}N_2O_4.H_2S_2.2H_2O$ and $C_{23}H_{26}N_2O_4.2H_2S_2$; these compounds were decomposed by acids giving a yellow oil which had the properties of H persulphide.

The composition of H persulphide cannot be regarded as settled; possibly more than one compound H_2SxS exists.

Preparation of H persulphide.—An aqueous solution of an alkaline polysulphide is slowly poured into excess of a solution of about equal parts of conc. hydrochloric acid and water; the liquid is placed in a filter in the neck of which oily drops collect, this oil is run off and dried over $CaCl_2$. To prepare the alkaline polysulphide, conc. KOHAq may be boiled with S; or 2 parts K_2CO_3 may be fused with 1 part S, the mass dissolved in water, boiled with excess of S, and allowed to clear; or 1 part CaO may be made into a thin cream with water and boiled with 2 parts S. As solution of polysulphides prepared as described may contain thiosulphates, Berthelot (*A. Ch.* [3] 49, 450) recommends to saturate KOHAq with H_2S out of contact with air, to add an equal volume of the same KOHAq, and to boil with S; or Na_2SO_4, or $CaSO_4$, may be strongly heated with powdered charcoal, the mass treated with water, and boiled with S. Sabatier (*C. R.* 100, 1346) thoroughly dries the oil, places it in a small flask with short neck connected with a bulb-tube surrounded by ice and having a pump attached; when the pressure is reduced to 40-100 mm. he heats the flask to 60°–80° in a water-bath.

Properties.—A yellow, mobile, oily liquid; S.G. 1·734 (Ramsay), 1·71 at 15° (Rebs). Odour is very irritating; taste bitter-sweet; the liquid raises blisters on the skin; it is soluble in C_6H_6, $CHCl_3$, and CS_2; decomposed by alkalis, alcohols, and slowly by ether; also by the action of light; slowly decomposed by $KMnO_4Aq$, Br, I, HNO_3Aq (Sabatier, *C. R.* 100, 1585). Hydrogen persulphide is more stable when the liquid contains some S or H_2S (Sabatier). When quite dry, the liquid may be preserved unchanged in a sealed tube (Bunsen, *P.* 46, 103); if the liquid is not quite dry, it slowly decomposes into crystals of S and liquid H_2S, if this change proceeds the tube may be broken by the pressure of the H_2S. Hydrogen persulphide is readily inflammable.

Reactions.—Hydrogen persulphide resembles H_2O_2 in its reactions; it is decomposed to H_2S and S by those substances which change H_2O_2 into H_2O and O, *e.g.* Pt, Au, Ag_2O, charcoal powder, &c.; it acts as a *reducing agent*, *e.g.* it decolourises indigo. *Water* decomposes it to H_2S and S, slowly at ordinary, quickly at higher temperatures. *Ammonia* causes a ppn. of S; *ether* acts slowly producing nacreous S; according to Sabatier (*l.c.*), *hydrochloric acid*, *dry air*, and *dry hydrogen* have no action.

Hydrogen telluride H_2Te (*Telluretted hydrogen. Tellurhydric acid. Hydrotelluric acid. Tellurium hydride*). Mol. w. 127. This compound, discovered by Davy (*G. A.* 37, 48, [1810]), resembles H_2S and H_2Se. It is formed by direct union of its elements, by heating Te in a stream of H (Löwe, *W. A. B.* 10, 727; Becker, *A.* 180, 257); also by decomposing ZnTe by dilute HClAq. Berthelot a. Fabre (*A. Ch.* [6] 14, 103) recommend the use of MgTe, prepared by action of excess of Te vapour on heated Mg in an atmosphere of pure H; they decompose the MgTe in an atmosphere of pure N by very dilute HClAq. TeH_2 is a colourless gas, with disagreeable smell, which is different from that of H_2Se or H_2S; when inhaled, the effects are not so irritating as in the case of H_2Se (*q.v.*) (B. a. F., *l.c.*). TeH_2 is very unstable; it soon decomposes over dry Hg, even in the dark; in presence of moist air, decomposition is instantaneous (B. a. F., *l.c.*). TeH_2 is decomposed by heat; according to Ditte (*C. R.* 74, 980) this decomposition is less complete at higher than at lower temperatures; the behaviour is exactly similar to that of SeH_2 (*q.v.* p. 725). TeH_2 is readily combustible; it is fairly soluble in water, the solution is very quickly decomposed if exposed to air. Pure TeH_2 is rapidly and completely absorbed by solutions of alkalis, with production of alkali tellurides, if a trace of O is present the solution becomes violet or purple, and if much O is present Te is ppd. (B. a. F., *l.c.*). TeH_2 passed into solutions of metallic salts ppts. metallic tellurides. M. M. P. M.

HYDRO-HOMO-FERULIC ACID *v.* *m-Methyl derivative* of (4:3:1)-Di-oxy-phenyl-iso-butyric acid.

HYDROIODOANGELIC ACID *v.* Iodo-valeric acid.

HYDROIODOCINNAMIC ACID *v.* Iodo-phenyl-propionic acid.

(α)-**HYDROJUGLONE** $C_{10}H_8O_3$. *Oxy-(α)-hydro-naphthoquinone?* [170°]. S. (at 25°) = ·5. Occurs, together with about $\frac{1}{5}$ as much (β)-hydrojuglone, in the leaves and unripe green shells of the walnut. Formed by reduction of juglone (Mylius, *B.* 17, 2411; 18, 475, 2567). Colourless plates or needles. V. e. sol. alcohol, ether, and acetic acid, nearly insol. benzene and petroleum-ether, insol. chloroform. It dissolves in aqueous NaOH with a yellow colour, which almost instantly becomes violet on exposure to air from formation of juglone. It is odourless, but possesses a burning taste, and is poisonous; $\frac{1}{2}$ g. killed a rabbit in 2 hours. By treatment with acid anhydrides it is converted into the alkoyl derivatives of (β)-hydrojuglone. On heating (α)-hydrojuglone above its melting-point it is converted into the (β)-isomeride. On the other hand the inverse change takes place if (β)-hydrojuglone is boiled with dilute HCl for a long time. Potash-fusion gives *m*-oxy-benzoic acid, together with phenol, salicylic acid, and pyrocatechin. Oxidising agents very readily convert it into juglone. On distillation with zinc-dust it gives *naphthalene.*

Tri-acetyl derivative $C_{10}H_5(OAc)_3$ [124°].

(β)-Hydrojuglone $C_{10}H_8O_3$. *Tri-oxy-naphthalene?* [97°]. S. (at 25°) = ·11. Occurs, together with about 5 times as much (α)-hydrojuglone, in the unripe shells of the walnut Silvery six-sided tables or flat needles. V. sol. chloroform and benzene, sl. sol. cold alcohol and ether. Volatile with steam. Aromatic smell and burning taste. Formed by heating (α)-hydrojuglone above its melting-point. Converted into the (α)-hydrojuglone by long boiling with dilute HCl. Dissolves in alkalis with a yellow colour, which becomes red on exposure to the air. Fe_2Cl_6 gives a blood-red colouration. It is not oxidised to juglone, except under conditions which allow of its previous conversion into (α)-hydrojuglone. Its alkoyl derivatives are formed by the action of anhydrides upon either (α)- or (β)-hydrojuglone.

Tri-acetyl derivative $C_{10}H_5(OAc)_3$: [130°]; colourless prisms (from alcohol).

Tri-benzoyl derivative $C_{10}H_5(OBz)_3$: [129°]; colourless needles, sl. sol. alcohol and acetic acid, insol. water (Mylius, *B.* 18, 2567).

HYDROLUTIDINE *v.* *Di-hydride* of Di-methyl-pyridine.

HYDROMECONIC ACID *v.* Meconic acid.

HYDROMELLITIC ACID *v.* *Hexahydride* of Mellitic acid.

HYDRO-METHYL-KETOLE *v.* Methyl-indole *dihydride.*

HYDRO-METHYL-PYRIDINES *v.* *Hydrides* of Methyl-pyridines.

DI-HYDRO-TRI-METHYL-PYRIDINE DI-CARBOXYLIC ETHER *v.* *Di-hydride* of Tri-methyl-pyridine di-carboxylic ether.

HYDRO-METHYL-PYRROLE *v.* *Hydride* of Methyl-pyrrole.

HYDRO-METHYL-QUINALDINES *v.* *Hydrides* of Di-methyl-quinolines.

HYDRO-MUCONIC ACID $C_6H_8O_4$ *i.e.* $(CO_2H).CH:CH.CH_2.CH_2(CO_2H)$. [195°]. S. ·9 at 16°. Formed by partial reduction of diacetylene-di-carboxylic acid with sodium-amalgam. On further reduction it gives adipic acid (Baeyer, *B.* 18, 680). Formed also by treating dichloro-muconic acid $C_6H_4Cl_2O_4$ with sodium-amalgam (Bode, *A.* 132, 98). Colourless prisms; v. sl. sol. cold water, v. sol. hot water and alcohol, m. sol. ether. Reduced by sodium-amalgam to adipic acid (Limpricht, *A.* 165, 263). By treatment with bromine it may be converted into bromo-hydromuconic acid [183°], di-, tri-, and tetra-, bromo-adipic, and iso-di-bromo-adipic acids.—ZnA″.—Ag_2A''.

Anhydride $C_6H_6O_3$. Trimetric crystals; *a*:*b*:*c* = ·206:1:·332 (Fock, *Z. K.* 7, 48).

HEXA-HYDRO-NAPHTHALENE *v.* Naphthalene hexahydride.

TETRA-HYDRO-NAPHTHALENE DI-CARBOXYLIC ACID *v.* *Tetrahydride* of Naphthalene di-carboxylic acid.

‘**DIHYDRONAPHTHOIC ACID**’ so-called *v.* Methyl-indonaphthene-carboxylic acid.

(α)-**HYDRO-NAPHTHOQUINONE** $C_{10}H_8O_2$ *i.e.* $C_{10}H_6(OH)_2$[1:4]. [173°] (P.); [176°] (G.). Formed by the action of fuming HIAq on (α)-naphthoquinone (Groves, *A.* 167, 359); or, better, from (α)-naphthoquinone, tin, and HClAq (Plimpton, *C. J.* 37, 635). A small quantity may be obtained by heating (α)-naphthoquinone with aqueous SO_2 at 150° (Plimpton). White needles; m. sol. boiling water, v. sol. boiling alcohol, ether, and HOAc, sl. sol. hot benzene, almost insol. CS_2 and ligroïn. Oxidising agents convert it into (α)-naphthoquinone; with a solution of (α)-naphthoquinone it forms dark-purple crystals of the quinhydrone $C_{20}H_{14}O_4$.

Di-acetyl derivative $C_{10}H_6(OAc)_2$. [c. 130°]. Easily soluble tables (from alcohol) (Korn, *B.* 17, 3025).

(β)-Hydro-naphthoquinone $C_{10}H_6(OH)_2$[1:2]. [c. 60°]. Formed by treating (β)-naphthoquinone with cold conc. SO_2Aq (Liebermann a. P. Jacobson, *A.* 211, 58). Silvery plates. It dissolves in aqueous alkalis forming yellow solutions which turn deep green in the air. Violently inflames the skin.

Di-acetyl derivative $C_{10}H_6(OAc)_2$. [c. 106°]. Very soluble plates (from HOAc) (Korn, *B.* 17, 3025).

Isohydronaphthoquinone? $C_{10}H_8O_2$. Formed by the action of water (30 pts.) on the compound $C_{10}H_8(HOCl)_2$ (so-called di-chloro-naphthydrene glycol) at 150° (Grimaux, *Bl.* [2] 19, 397). Small needles; sol. water and ether, insol. $CHCl_3$ and benzene. Its alkaline solutions turn red in the air. It reduces ammoniacal $AgNO_3$. $FeCl_3$ gives, in its aqueous solution, a brown pp. sol. alkalis.

HYDRO-o-OXY-BENZ-AMIDE v. Tri-oxy-hydrobenzamide.

HYDRO-OXY-CAMPHORONIC ACID v. Camphor.

HYDRO-OXY-METHYL-QUINOLINE v. *Hydride* of Oxy-methyl-quinoline.

DI-HYDRO-OXY-QUINOLINE v. *Hydro-carbostyril* under Amido-phenyl-propionic acid; v. also *Hydride* of Oxy-quinoline.

HYDRO-PHENOL-PHTHALIDIN CHLORIDE v. Di-chloro-phenyl-anthranol dihydride.

HYDRO-PHENYL-ACRIDINE v. Phenyl-acridine *hydride.*

HYDRO-PHENYL-CROTONIC ACID v. Phenyl-butyric acid.

TETRA-HYDRO-PHENYL-QUINOLINE v. *Tetra-hydride* of Phenyl-quinoline.

HYDROPHLORONE v. Hydroxyloquinone.

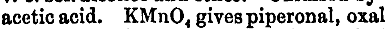
HYDROPHTHALIC ACIDS v. *Hydrides* of Phthalic acid.

HYDRO-PICOLINE v. *Hydride* of Methyl-pyridine.

HEXA-HYDRO-PICOLINIC ACID v. *Hexa-hydride* of Pyridine carboxylic acid.

HYDRO-PIPERIC ACIDS $C_{12}H_{12}O_4$. (α) [78°]. (β) [131°]. By reduction of piperic acid by sodium-amalgam two hydro-piperic acids are got. They may be separated by crystallisation from alcohol, when the (β)-acid separates first. The (α)-acid is the chief product (Foster, *A.* 124, 117; Fittig a. Mielck, *A.* 152, 56). The (β)-acid forms thin needles (from alcohol). Its ammonium salt is more soluble than that of the (α)-acid. The (β)-acid is only formed when the liquid becomes very alkaline, if the alkali be constantly neutralised during the reduction only (α)-acid is got. The (α)-acid may be converted into the (β)-acid by heating with (10 pts. of) dilute (10 p.c.) NaOH 9 hours at 100° (Lorenz, *B.* 14, 785; Fittig a. Buri, *A.* 216, 171; 227, 31; Weinstein, *A.* 227, 32). Br in CS_2 converts the (α)-acid into its dibromide, di-bromo-piperhydronic acid $C_{12}H_{12}Br_2O_4$ [137°-140°], while the (β)-acid gives a product of substitution, bromo-hydro-piperic acid [171°]. The (β)-acid is reduced by sodium amalgam in neutral solution to piper-hydronic acid, while the (α)-acid is not reduced thereby.

(α)-Hydropiperic acid

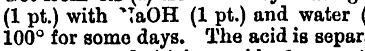


$CH_2{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}C_6H_3.CH_2.CH{:}CH.CH_2.CO_2H$? [78°].

Thin needles (from hot water); sl. sol. hot water, v. e. sol. alcohol and ether. Oxidised by CrO_3 to acetic acid. $KMnO_4$ gives piperonal, oxalic acid, and di-oxy-piperhydronic acid $CH_2O_2C_{11}H_{12}O_4$ (Riegel, *B.* 20, 415). Not attacked by AcCl at 100°. Potash-fusion gives protocatechuic acid and HOAc.

Salts.—NH_4A': small laminæ.—KHA'_2: amorphous, formed by adding K_2CO_3 to an alcoholic solution of the acid. Decomposed by water. —AgA': crystalline pp.

(β)-Hydro-piperic acid



$CH_2{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}C_6H_3.CH_2.CH_2.CH{:}CH.CO_2H$? [131°].

Got from its (α)-isomeride by heating this acid (1 pt.) with NaOH (1 pt.) and water (9 pts.) at 100° for some days. The acid is separated from undecomposed (α)-isomeride by crystallisation from alcohol (90 p.c.). Thin needles (from alcohol); less soluble than its isomeride in the usual menstrua. Bromine forms a substitution, not an addition, product. $KMnO_4$ oxidises it to di-oxy-piperhydronic acid $CH_2O_2C_{11}H_{12}O_4$ and methyl-anhydro-caffeic acid $CH_2O_2C_9H_8O_2$.

HYDROPYRENEQUINONE v. Pyrene.

DIHYDROPYRIDINE v. Pyridine dihydride.

HYDRO-PYRO-CINCHONIC ACID v. Di-methyl-succinic acid.

HYDROPYROMELLITIC ACID v. Pyromellitic acid.

DIHYDROPYRROLE v. Pyrrole dihydride.

TETRA-HYDRO-QUINALDINE v. (*Py.* 3)-Methyl-quinoline tetrahydride.

HYDROQUINANISOL v. *Methyl ether* of Oxy-quinoline-tetra-hydride.

HYDROQUINICINE v. Cinchona bases.

HYDROQUINIDINE v. Cinchona bases.

HYDROQUININE v. Cinchona bases.

HYDROQUINOLINE v. Quinoline hydride.

TETRA-HYDRO-QUINOLINE HYDRAZINE v. Amido-tetra-hydro-quinoline.

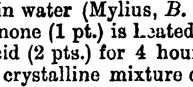
HYDROQUINONE $C_6H_6O_2$ *i.e.* $C_6H_4(OH)_2$[1:4]. *p-Di-oxy-benzene. Quinol. Pyrogentisic acid.* Mol. w. 110. [169°] (Hlasiwetz a. Habermann, *B.* 8, 684). S.G. 1·326 (Schröder, *B.* 12, 563). H.F. (from diamond) 86,100 (Berthelot a. Louguinine, *A. Ch.* [6] 13, 337; *C. R.* 104, 1576); 100,880 (Stohmann, *J. pr.* [2] 33, 471). S. 6·21 at 15°; 10·44 at 28·5°.

Formation.—1. By the reduction of quinone, and by the dry distillation of quinic acid (Wöhler, *A.* 51, 152).—2. From arbutin by boiling with dilute H_2SO_4, or by the action of emulsin (Kawalier, *A.* 84, 358; Strecker, *A.* 107, 229).—3. By boiling *p*-diazo-phenol sulphate with dilute (12 p.c.) H_2SO_4, and extracting the cooled product with ether. The yield amounts to 46 p.c. (Weselsky a. Schuler, *B.* 9, 1159). In like manner hydroquinone may be obtained by the action of water at 140° on [4:1]$C_6H_4(OMe).N{:}N.SO_3H$, derived from the methyl ether of *p*-nitro-phenol (H. Salkowski, *B.* 7, 1010).—4. By gently heating a dilute solution of nitroso-phenol in NaOHAq with hydroxylamine hydrochloride, nitrogen being given off (Hepp, *B.* 10, 1654).—5. From bromo-salicylic acid [4:1:2]$C_6H_3Br(OH)(CO_2H)$ by fusion with NaOH, and heating the resulting di-oxy-benzoic acid [197°] in a bath of H_2SO_4 at 215°, when pure hydroquinone sublimes (Rakowski a. Leppert, *B.* 8, 788; *cf.* Demole, *B.* 7, 1441; Hlasiwetz, *A.* 175, 67).—6. By passing a current of air for 3 hours through an alkaline solution of succinylo-succinic ether, and heating the resulting di-oxy-terephthalic acid with KOH (Herrmann, *B.* 10, 107).—7. A product of the distillation of succinates (Von Richter, *J. pr.* [2] 20, 207). 8. By passing a rapidly alternately electric discharge through a solution of phenol (*q. v.*).—9. From *p*-iodo-phenol by potash-fusion (Körner, *Z.* 1866, 662, 731).—10. Occurs in the urine of dogs that have taken benzene (Baumann, *H.* 6, 190), phenol (Baumann a. Preusse, *B.* 12, 706), or arbutin (Mering, *Ar. Physiol.* 62, 276).

Preparation.—Aniline (1 pt.) is dissolved in H_2SO_4 (8 pts.) diluted with water (30 pts.), and to this solution, after cooling, powdered $K_2Cr_2O_7$ (3½ pts.) is gradually added, too great a rise of temperature being avoided. The thick pulpy mass of aniline-black produced at first changes after a time to a dirty-brown solution, which is then treated with excess of SO_2, boiled with animal charcoal, filtered, and shaken with ether. The ethereal extract when distilled leaves hydroquinone (Nietzki, *B.* 10, 1934; 19, 1468; *A.* 215, 128; Ekstrand, *B.* 11, 713).

Properties.—Dimorphous, crystallising by sublimation in monoclinic plates; $a:b:c = 2{\cdot}605:1:1{\cdot}558$; $\beta = 73°$; and from aqueous solutions in hexagonal prisms; $a:c = 1:{\cdot}659$ (Lehmann, *Z. K.* 1, 44; Groth, *B.* 3, 450). Has a slightly sweet taste. V. sol. alcohol, ether, and hot water, v. sl. sol. cold benzene, may be distilled. When $FeCl_3$ is added to its aqueous solution there is formed a mass of lustrous dark green spangles of quinhydrone, and at the same time the odour of quinone is apparent. A further addition of $FeCl_3$ converts the quinhydrone into quinone, the crystals redissolving. Silver nitrate gives a brownish-white pp., and, on warming, reduction to black metallic silver takes place. Hydroquinone reduces a boiling acidulated solution of $KMnO_4$, 1 molecule of hydroquinone requiring 10 atoms of oxygen. Its reducing power is intermediate between that of pyrocatechin and that of resorcin (Dreyfus, *C. R.* 105, 523). Hydroquinone reduces Fehling's solution, even in the cold. An aqueous solution of hydroquinone slowly turns brown when exposed to the air, losing its reducing power. An alkaline solution turns brown much more rapidly. Lead acetate gives no pp. in dilute solutions, but if hydroquinone be dissolved in a moderately concentrated warm aqueous solution of lead acetate prisms of $C_6H_6O_2Pb(OAc)_2\,1\frac{1}{2}aq$ separate on cooling (Wöhler, *A.* 69, 299). Hydroquinone prevents the alkaline fermentation of urine (Andraeff, *Vrach*, 1887, 230).

Reactions.—1. *Oxidised* to quinone by $FeCl_3$, chlorine, dilute HNO_3, and chromic acid.—2. By passing through a *red-hot tube* it is split up into quinone and hydrogen (Hesse, *A.* 114, 297).—3. *Hydroxylamine* in acid solution gives the di-oxim of quinone.—4. Strong *nitric acid* decomposes hydroquinone in the cold, forming oxalic acid and HCy (Nietzki, *A.* 215, 138).—5. *Nitrous acid gas* passed into an ethereal solution of hydroquinone at 0° forms small golden needles of di-nitro-di-oxy-quinone (Nietzki, *B.* 10, 2147).—6. Not affected by *potash-fusion* (Wölz, *A.* 168, 91). *Soda-fusion* converts it into (1,2,4)-tri-oxy-benzene, (δ)-hexa-oxy-diphenyl, and tetra-oxy-diphenyl $C_{12}H_{10}O_4$ (Barth a. Schreder, *M.* 4, 176; 5, 589).—7. When heated with PCl_5 it appears to form first $C_6H_4(OH)(OPCl_2)$ and then $C_6H_4(OPCl_2)_2$ (Scheid, *A.* 218, 207). 8. H_2S passed into a cold saturated solution of hydroquinone forms colourless rhombohedra $(C_6H_6O_2)_3H_2S$ decomposed by boiling water into its components (Wöhler, *A.* 69, 297). H_2S passed into a solution of hydroquinone saturated at 40° forms long prisms of $(C_6H_6O_2)_4H_2S$.—9. SO_2 passed into a cold saturated solution of hydroquinone forms yellow rhombohedra $(C_6H_6O_2)_3SO_2$, which quickly decompose (Clemm, *A.* 110, 357; Hesse, *A.* 114, 300).—10. *Aldehyde* in presence of dilute HCl forms a resin on heating (Michael a. Ryder, *Am.* 9, 133).—11. With *acetone* it forms an unstable compound $C_6H_6O_2C_3H_6O$, which forms triclinic crystals, decomposed into its components by solution in alcohol, acetone, or hot water, and even by exposure to air (Habermann, *M.* 5, 529).—12. HCy forms needles $(C_6H_6O_2)_3HCy$ decomposed by heat or by water into its components (Mylius, *B.* 19, 1008).—13. *Aniline* when boiled with hydroquinone forms $C_6H_6O_2(NH_2Ph)_2$, which crystallises in large plates [90°], sol. alcohol and hot water. Its solution on exposure to the air is oxidised to quinone dianilide. By boiling with benzene it is resolved into hydroquinone and aniline (Hebebrand, *B.* 15, 1973). Hydroquinone (1 mol.) heated with aniline (4 mols.) and $CaCl_2$ at 250° gives $C_6H_4(OH)(NHPh)$ [70°] (Calm, *B.* 16, 2786). In like manner *o-toluidine* and $CaCl_2$ at 245° give $C_6H_4(OH)(NHC_7H_7)$ [90°].—14. *p-Toluidine* forms $C_6H_6O_2(C_7H_7NH_2)_2$ [98°] (Hebebrand, *B.* 15, 1974).—15. By heating with *phenyl cyanate* at 100° there is formed $C_6H_4(O.CO.NHPh)_2$, which crystallises from alcohol in prisms [c. 207°]. It is insol. benzene. At its melting-point it begins to decompose into phenyl cyanate and hydroquinone (Snape, *C. J.* 47, 772).—16. *Chloroformic ether* $ClCO_2Et$ acting on sodium hydroquinone forms *p*-phenylene di-carbonic ether $C_6H_4(O.CO_2Et)_2$. This crystallises from alcohol in long needles, [100°], (310°), and appears to be split up by heat into CO_2 and mono-ethyl hydroquinone (215°-250°) (Bender, *B.* 13, 696; Wallach, *A.* 226, 85).—17. *Chloro-formamide* gives $C_6H_4(O.CONH_2)_2$, which crystallises from alcohol in small needles [236°].—18. Heated with $ZnCl_2$ and *glacial acetic acid* it gives di-oxy-phenyl methyl ketone (Nencki a. W. Schmid, *J. pr.* [2] 23, 546).—19. *Di-chloro-di-ethyl oxide* in warm EtOAc forms $C_6H_3(OH)_2.CH_2.CH(C_6H_3(OH)_2)_2$, an amorphous substance, sol. alcohol, acetone, HOAc, and alkalis, and forming a hexa-acetyl derivative. $FeCl_3$ converts it into a green colouring matter $C_{20}H_{16}O_6$, whence bromine forms $C_{20}H_7Br_9O_6$. When an excess of di-chloro-di-ethyl oxide acts on a solution of hydroquinone in EtOAc there is formed a resin and a soluble compound $C_{16}H_{13}ClO_4$ (Wislicenus a. Siegfried, *A.* 243, 171).—20. *Formic acid* forms a compound $(C_6H_6O_2)_4CH_2O_2$, which crystallises in needles, and melts at 60°, giving off formic acid. It is also decomposed into its constituents by solution in water (Mylius, *B.* 19, 1003). When hydroquinone (1 pt.) is heated with crystallised formic acid (2 pts.) for 4 hours at 250° there is formed a crystalline mixture of $(C_6H_6O_2)_4CH_2O_2$ and an anhydride thereof. The anhydride $(C_6H_6O_2)_3C_2H_2O_3$ crystallises in colourless glassy needles, split up by water, alcohol, or ether, into CO, formic acid, and hydroquinone (Mylius, *B.* 19, 999).—21. $KHCO_3$ (4 pts.) heated in a digestor with hydroquinone (1 pt.) and water (4 pts.) forms di-oxy-benzoic acid, the yield being about 20 p.c. (Senhofer a. Sarlay, *M.* 2, 449).—22. *Malic acid* and H_2SO_4 form oxy-coumarin



$$\begin{array}{l}\text{CHCH.}\,\text{—CO.—CO}\\ |\qquad\qquad\quad\ \ \|\qquad\ \ |\\ \text{C(OH):CH.C.CH:CH}\end{array}$$

[250°] (Von Pechmann a. Welsh, *B.* 17, 1640).—23. With KOH and $K_2S_2O_7$ it forms potassium oxy-phenyl sulphate $C_6H_4(OH)SO_4K$ crystallising in trimetric tables (Baumann, *B.* 11, 1913).

Acetyl derivative $C_6H_4(OAc)_2$. [121°]. Formed, slowly, by the action of AcCl on hydroquinone in the cold (Nietzki, *B.* 11, 470). Formed also by heating quinone with NaOAc and Ac_2O or glacial HOAc at 100° (Hesse, *A.* 220, 365), or by heating quinone with Ac_2O at 260° (Sarauw, *A.* 209, 128). Long needles (from alcohol), plates, or tables. V. sol. benzene, chloroform, and ether, m. sol. alcohol and hot water. May be sublimed. Split up by long boiling with water into HOAc and hydroquinone. If it be treated with PCl_5 and the product distilled with steam, white needles of $C_8Cl_3H_5O_2$ [66°] are got (Michael, *Am.* 9, 211). This body, which may be $C_6H_4(OH)(OCCl{:}CCl_2)$, is sl. sol. hot water, sol. cold ether, benzene, and alcohol. It dissolves in alkalis and is reppd. by acids. With AcCl it gives an acetyl derivative.

Propionyl derivative $C_6H_4(OC_3H_5O)_2$. [113°]. Large plates (from alcohol); v. sol. chloroform and ether, sl. sol. hot water (Hesse, *A.* 200, 246). Gives a nitro- derivative [86°].

Benzoyl derivative $C_6H_4(OBz)_2$. [199°]. Silky needles (from benzene); v. sl. sol. boiling alcohol (Dœbner, *A.* 210, 263).

Methyl ether $C_6H_4(OH)(OMe)$. [53°]. (242°). Formed, together with hydroquinone, by boiling arbutin with dilute H_2SO_4; formed also, together with the di-methyl ether, by heating hydroquinone with KOH and $KMeSO_4$ at 170° (Hlasiwetz a. Habermann, *A.* 177, 338). Prepared by heating hydroquinone (2 pts.) with KOH (1 pt.), MeI (3 pts.), and some MeOH at 110° (Hesse, *A.* 200, 254). Flat white needles (Tiemann, *B.* 14, 1989) or trimetric plates. Not volatile with steam (difference from the di-methyl ether). V. sol. cold benzene (difference from hydroquinone). Sol. boiling water. $FeCl_3$ converts it into quinhydrone. It reduces hot ammoniacal $AgNO_3$. Fuming HNO_3 dissolved in ether forms a mono- and a di-nitro- derivative, melting at 83° and 102° respectively (Weselsky a. Benedikt, *Sitz. W.* [2] 84, 258).—$C_6H_4(OMe)(OK)$: crystalline powder; insol. ether (Michael, *Am.* 5, 177).

Di-methyl ether $C_6H_4(OMe)_2$. [56°]. H.F.p. 81,924 ($C,O_2 = 94{,}000$; $H_2,O = 69{,}000$) (Stohmann, *J. pr.* [2] 35, 28). Formed by boiling hydroquinone (78 g.) under 960 mm. pressure, with KOH (93 g.), and MeI (234 g.) dissolved in MeOH (Mühlhäuser, *A.* 207, 252). Large plates. Reduces hot ammoniacal $AgNO_3$. $FeCl_3$ forms quinhydrone.

Mono-ethyl ether $C_6H_4(OEt)(OH)$. [66°]. (247°). From the ethyl derivative of the sulphate of diazo-phenol by boiling with water and extracting with ether (Hantzsch, *J. pr.* [2] 22, 464). Also from hydroquinone, KOH, and MeI (Wichelhaus, *B.* 12, 1501). Thin plates (from water). Sl. sol. cold water; v. sol. hot water, alcohol, and ether. Slightly volatile with steam. Boiled with dilute hydric iodide and a little alcohol it forms hydroquinone. Conc. HI at high temperatures carbonises it. Although hydroquinone forms no aldehyde by Tiemann a. Reimer's method, yet ethyl-hydroquinone (14 g.) with NaOH (20 g.) and water (35 g.) at 60° is converted into a di-oxy-benzoic aldehyde by running in chloroform (15 g.).

Di-ethyl ether $C_6H_4(OEt)_2$. [124°]. From hydroquinone, NaOH, and EtI (Nietzki, *A.* 215, 145). Plates; volatile with steam. V. sol. alcohol, ether, chloroform, and benzene.

Methyl ethyl ether $C_6H_4(OMe)(OEt)$. [39°]. Prepared by heating the mono-methyl ether with $KEtSO_4$ and KOH, and distilling the product (Fiala, *M.* 5, 232). Colourless crystalline mass, smelling like oil of fennel. Insol. water, sol. benzene and ether.

Methyl propyl ether $C_6H_4(OMe)(OPr)$. [24°]. From the mono-methyl ether, KOH, and potassium propyl sulphate. Purified by frequent distillation with steam (F.). Leaflets; insol. water, sol. benzene, ether, and alcohol.

Ethyl propyl ether $C_6H_4(OEt)(OPr)$. [36°]. Pearly plates (from HOAc).

Methyl isobutyl ether $C_6H_4(OMe)(OCH_2Pr)$. (227°–230°). From $C_6H_4(OH)(OMe)$, KOH, and potassium isobutyl sulphate. Purified by fractional distillation. Heavy oil, with aromatic odour; sol. benzene, ether, and alcohol (F.).

Ethyl isobutyl ether $C_6H_4(OEt)(OCH_2Pr)$. [39°]. Laminæ (Fiala, *M.* 6, 910).

Propyl isobutyl ether $C_6H_4(OPr)(OCH_2Pr)$. (245°). Oil.

Di-isobutyl ether $C_6H_4(OCH_2Pr)_2$. (262°). Formed by heating hydroquinone with KSO_4CH_2Pr and KOH in sealed tubes at 150°, being isolated by distilling the product with steam (Schubert, *M.* 3, 680). Leaflets; insol. water, sol. alcohol and ether. Chlorine forms a di- and a tetra-chloro- derivative, together with tetra-chloro-quinone. Bromine forms a di-bromo-derivative as well as tetra-bromo-quinone. A mixture of HNO_3 and H_2SO_4 forms a tetra-nitro-derivative. All these derivatives are crystalline, insol. water, and sol. alcohol and ether.

Methyl isoamyl ether $C_6H_4(OMe)(OCH_2.CH_2Pr)$. (234°–237°). Oil (Fiala, *M.* 6, 910).

Ethyl isoamyl ether $C_6H_4(OEt)(OCH_2.CH_2Pr)$. (252°). Oil.

Benzyl derivative $C_6H_5CH_2.O.C_6H_4OH$. [122·5°]. Formed from benzyl-arbutin (*v.* ARBUTIN) by boiling dilute H_2SO_4 (Schiff a. Pellizzari, *A.* 221, 369). Formed also from hydroquinone, KOH, alcohol, and benzyl bromide. Silvery scales (from water). V. sl. sol. cold water; v. sol. alcohol, ether, and benzene. Sol. KOHAq. HNO_3 forms a di-nitro- derivative [137°].

Di-benzyl derivative $C_{20}H_{18}O_2$ *i.e.* $C_6H_4(O.C_7H_7)_2$. [130°] (S. a. P.); [128°] (Colson, *Bl.* [3] 1, 347). From hydroquinone, KOH, benzyl bromide, and alcohol. Tables (from alcohol). Insol. water and KOHAq; sol. benzene, ether, and chloroform. Conc. HNO_3 dissolves it, forming a nitro- derivative crystallising in lemon-yellow needles $C_{20}H_{17}(NO_2)O_2$. [85°] (S. a. P.); [78°] (C.).

Bromo-phenyl ether $C_6H_4(OH)(OC_6H_4Br)$. Formed by the action of boiling HBr on a solution of *p*-diazo-phenol sulphate:

$$\begin{gathered}
\text{(i.) } C_6H_4(OH)N_2SO_4H + HBr \\
= C_6H_4(OH)Br + N_2 + H_2SO_4 \\
\text{(ii.) } C_6H_4(OH)Br + C_6H_4(OH)N_2SO_4H \\
= C_6H_4(OH).O.C_6H_4Br + H_2SO_4 + N_2.
\end{gathered}$$

A pungent oil. Sol. alkalis, alcohol and ether. Its constitution is somewhat doubtful, as its vapour density has not been taken (Böhmer, *J. pr.* [2] 24, 473).

References.—AMIDO-, BROMO-, CHLORO-, IODO- and NITRO-, HYDROQUINONE.

Dihydroquinone *v.* TETRA-OXY-DIPHENYL.

HYDROQUINONE CARBOXYLIC ACID *v.* DI-OXY-BENZOIC ACID.

Hydroquinone di-carboxylic acid *v.* DI-OXY-TEREPHTHALIC ACID.

Hydroquinone tetra-carboxylic acid $C_{10}H_6O_{10}$ *i.e.* $C_6H_4(OH)_2(CO_2H)_4$ [1:4:2:3:5:6]. *Di-oxy-pyromellitic acid.* Obtained by saponifying the ether with KOHAq (Nef, *A.* 237, 32; *C. J.* 53, 428). Flat, pale yellow, needles (containing 1½ aq), v. sol. hot water, the yellow solution exhibiting green fluorescence. $FeCl_3$ colours its solution blue. Nitric acid does not act on it in the cold, but on warming complete decomposition occurs. Chromic acid behaves in like manner. Na_4A^{iv}: characteristic faint yellow prisms, v. sl. sol. NaOHAq.—Ag_4A^{iv}: lemon yellow flocculent pp. The lead salt is a light yellow granular pp. The barium salt is a pale yellow granular pp.

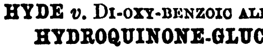
Ethyl ether Et_4A^{iv}. [128°]. Formed by treating a solution of quinone tetra-carboxylic ether in HOAc with zinc-dust (Nef). Pale yellow needles, v. sol. alcohol, ether, and HOAc, the solutions exhibiting blue fluorescence. Crystallises in two forms, both monoclinic, viz.: (i.) $a:b:c = 2{\cdot}388:1:3{\cdot}060$; $\beta = 64° 36'$; and (ii.) $a:b:c = 1{\cdot}790:1:3{\cdot}321$; $\beta = 81° 53'$ (Groth). Its alcoholic solution is coloured bluish-green by $FeCl_3$. It dissolves in dilute NaOHAq. NaOEt gives a red colour. Nitric acid (S.G. 1·4) oxidises it to quinone tetra-carboxylic ether. Zinc and HCl reduce it to the following body.

Dihydride of hydroquinone tetracarboxylic ether $C_{18}H_{24}O_{10}$ *i.e.* $C_6H_2(OH)_2(CO_2Et)_4$. *p-Diketo-methylene tetracarboxylic acid.* [144°]. Formed by adding zinc-dust (10 g.) and conc. HCl to an alcoholic solution of the preceding ether (2 g.) (Nef). Colourless needles or prisms (containing *x*aq). In the hydrated condition it is v. sol. alcohol and ether; in the anhydrous condition it is but slightly soluble in these liquids. Its solutions show feeble blue fluorescence. Its alcoholic solution is coloured cherry-red by $FeCl_3$. Bromine added to its solution in CS_2 forms hydroquinone tetra-carboxylic ether. It reacts with phenyl-hydrazine and with hydroxylamine; and on this account its formula may also be written $C_6H_4O_2(CO_2Et)_4$ *i.e.* tetra-hydride of quinone tetra-carboxylic acid. Hence Nef suggests that one of the two crystalline forms in which he obtained hydroquinone tetra-carboxylic ether may be the di-hydride of quinone tetra-carboxylic ether $C_6H_2O_2(CO_2Et)_4$.

HYDROQUINONE CARBOXYLIC ALDEHYDE *v.* DI-OXY-BENZOIC ALDEHYDE.

HYDROQUINONE-GLUCOSIDE *v.* ARBUTIN.

HYDROQUINONE-PHTHALEÏN $C_{20}H_{12}O_5$ *i.e.*



$CO{<}{\begin{smallmatrix}C_6H_4\\O\end{smallmatrix}}{>}C{<}{\begin{smallmatrix}C_6H_3(OH)\\C_6H_3(OH)\end{smallmatrix}}{>}O$. Mol. w. 332.

[227°]. Formed, together with quinizarin, by heating hydroquinone (2 mols.) with phthalic anhydride (1 mol.) and a quantity of $SnCl_4$ equal to 13 times the weight of the mixture, the whole being heated at 125° for 13 hours (Grimm, *B.* 6, 506; Ekstrand, *B.* 11, 713). Tables (containing aq from water) or needles (from ether); sl. sol. hot water, v. sol. alcohol and ether. Crystallises from alcohol in needles (containing HOEt). Alkalis turn its aqueous solution deep violet. Bromine, added to its solution in HOAc, forms penta-bromo-hydroquinone phthaleïn $C_{20}H_7Br_5O_5$ [above 300°], a colourless crystalline powder, insol. all ordinary solvents. It gives colourless solutions with alkalis.

Di-acetyl derivative $C_{20}H_{10}Ac_2O_5$. [210°]. Colourless crystals (from MeOH).

Hydroquinone phthalin $C_{20}H_{14}O_5$. [203° uncor.]. Formed by heating hydroquinone-phthaleïn for 4 hours with zinc-dust and aqueous NaOH. Crystallises from benzene in large tables (containing C_6H_6). Its alkaline solutions are colourless. H_2SO_4 forms a red liquid, whence water gives an olive-green flocculent pp. of hydroquinone-phthalidin, which dissolves in ether with green fluorescence. Hydroquinone-phthalin readily yields the corresponding phthaleïn when treated with oxidising agents.

Di-acetyl derivative $C_{20}H_{12}Ac_2O_5$. [191°]. Colourless prisms (from MeOH).

HYDRO-QUINONE SULPHONIC ACID $C_6H_3(OH)_2SO_3H$. Prepared by heating hydroquinone (1 pt.) with 8 pts. of H_2SO_4 at 50° for 3 hours (Seyda, *B.* 16, 688). Crystalline solid. Gives a blue colouration with Fe_2Cl_6. By fusion with NaOH or by heating to 180° with aqueous or alcoholic NH_3 the HSO_3 group is eliminated as sulphate and hydroquinone regenerated.

Salts.—A'K: long monoclinic crystals, $a:b:c = {\cdot}96:1:2{\cdot}2256$; $\beta = 107° 23'$; v. sol. water, sl. sol. alcohol; reduces $AgNO_3$.—A'_2Ba: amorphous powder, sol. water.—A'_2Zn 4aq: concentric needles, v. sol. water and alcohol.

Hydroquinone disulphonic acid $C_6H_2(OH)_2(SO_3H)_2$. Formed by treating quinic acid with fuming H_2SO_4 (Hesse, *A.* 110, 195). Syrup; v. sol. water and alcohol, insol. ether. Solutions of its alkaline salts give a deep blue colour with $FeCl_3$ and reduce $AgNO_3$. Converted into quinizarin by heating with phthalic acid and H_2SO_4. — K_2A'' 1½aq: prisms. — CaA'' 3aq. — BaA'' 4aq: monoclinic prisms, m. sol. cold water. —$A''(PbOH)_2$.

Hydroquinone-di-sulphonic acid $C_6H_2(OH)_2(SO_3H)_2$. Prepared by heating hydroquinone (1 pt.) with 5 pts. of fuming H_2SO_4 for 1 hour at 100°-110° (Seyda, *B.* 16, 690). Formed also by heating potassium thiochromate with water at 135° (Graebe, *A.* 146, 43). Long deliquescent needles. V. sol. alcohol, v. sl. sol. ether. Gives quinizarin when heated with phthalic acid and H_2SO_4.

Salts.—$A''K_2$ 4aq: long prisms, sol. hot water, sl. sol. cold water, insol. alcohol. $FeCl_3$ colours its aqueous solution blue. It reduces a boiling solution of $AgNO_3$.—$A''Na_2x$: white amorphous powder, sol. water, insol. alcohol.—A''Ba 3½aq: glistening needles or long prisms, sol. hot, sl. sol. cold, water, insol. alcohol.—A''Zn 6aq: concentric needles or long prisms, sol. hot water.

Hydroquinone di-sulphonic acid $C_6H_2(OH)_2(SO_3H)_2$. From *p*-diazo-phenol disulphonic acid (Wilsing, *A.* 215, 239). Does not crystallise. Gives with $FeCl_3$ a violet colour. Reduces $AgNO_3$. $BaCl_2$ and $Pb(OAc)_2$ give pps. sol. HOAcAq.

Salt.—K_2A''aq.

Hydroquinone-disulphonic acid. *Di-methyl derivative* $C_6H_2(OMe)_2(HSO_3)_2$. Prepared by sulphonating the di-methyl ether of hydroquinone (Kariof, *B.* 13, 1673). Colourless deliquescent needles. V. e. sol. water and alcohol, insol. ether.

Salts –A″K_2: large colourless tables, sol. water. $FeCl_3$ colours its solution deep violet-blue.—A″$(NH_4)_2$: colourless soluble prisms.—A″Ba: white amorphous powder, v. sol. water, insol. alcohol.—A″Zn: felted needles.

HYDRORETENEQUINONE *v.* Retene.

HYDROSORBIC ACID *v.* Hexenoic acid.

HYDROSULPHIDES. (*Sulphohydrates.*) Compounds of an element or radicle with hydrogen and sulphur. The name is sometimes restricted to those compounds which on account of their reactions probably contain the group SH. The hydrosulphides are the sulphur analogues of the hydroxides. The name *sulphohydrates*, sometimes given to these compounds, is badly chosen, as it suggests a compound of water with a sulphur-containing substance. The hydrosulphides are not numerous. Many non-metallic sulphides combine with more positive sulphides to form salts the negative radicle of which is the non-metallic sulphide; such salts may be regarded as derivatives of acidic hydrosulphides; but very few of these hypothetical acidic hydrosulphides have been isolated. As_2S_3, for instance, combines with many metallic sulphides to form salts of the three classes $As_2S_3.M^{I}_2S$, $As_2S_3.3M^{I}_2S$, and $As_2S_3.2M^{II}S$; the hydrosulphides of As corresponding to these salts would be $As_2S_4H_2$ or AsS.SH, $As_2S_6H_6$ or $As(SH)_3$, and $As_2S_5H_4$ or $As_2S(SH)_4$; but none of these hydrosulphides has been isolated. The compounds H.SH and $CS(SH)_2$ are acidic hydrosulphides. The metallic hydrosulphides which have been isolated, *e.g.* CaS_2H_2, BaS_2H_2, are few in number and on the whole unstable; the production of a hydrosulphide seems to be fairly characteristic of a markedly positive metal.

M. M. P. M.

HYDROSULPHOCYANIC ACID *v.* Cyanic (sulpho) acid, p. 303.

HYDRO-TEREPHTHALIC ACID *v. Hydrides* of Terephthalic acid.

HYDROTHYMOQUINONE $C_{10}H_{14}O_2$ *i.e.* $C_6H_2Me(C_3H_7)(OH)_2$. [140°]. (290°). Formed by reducing thymoquinone with SO_2 (Carstanjen, *J. pr.* [2] 3, 54; Lallemand, *A.* 101, 121; 102, 121). V. sl. sol. cold, m. sol. hot, water; v. sol. alcohol and ether. May be sublimed. Gives thymoquinone on oxidation. Its methyl ether constitutes 80 p.c. of the essential oil derived from the roots of *Arnica montana* (Sigel, *A.* 170, 363).

Sulphonic acid $C_6HMe(C_3H_7)(OH)_2.SO_3H$. **Potassium salt** KA′. Formed by warming thymoquinone with aqueous K_2SO_3 (Carstanjen, *J. pr.* [2] 15, 478). Crystalline. $FeCl_3$ colours its aqueous solutions emerald green, the colour changing to yellow. It reduces silver solution forming a mirror. Decomposed by boiling HClAq into H_2SO_4 and hydrothymoquinone.

HYDROTIGLIC ACID *v.* Valeric acid.

HYDROTIC ACID $C_5H_9NO_7$. A syrupy acid occurring in perspiration (Favre, *J. pr.* 58, 365). Sol. alcohol.—AgA′: v. sl. sol. alcohol.

HEXA-HYDRO-TOLUENE *v.* Toluene hexahydride.

HYDROTOLUQUINONE $C_6H_3Me(OH)_2$[1:2:5]. [124°]. (N.); [126°] (Riedel, *B.* 13, 126).

Formation.—1. By reducing toluquinone with SO_2 (Nietzki, *A.* 215, 159).—2. By oxidising *o*-toluidine with chromic acid mixture (Nietzki, *B.* 10, 1935).—3. By treating amido-*o*-cresol with nitrous acid (Nevile a. Winther, *C. J.* 41, 415; *B.* 15, 2979). Pearly plates. May be sublimed. V. e. sol. water, alcohol and ether, m. sol. benzene. Oxidised readily to toluquinone. In aqueous NaOH it forms a bluish-green solution, turning dark brown. Its ammoniacal solution turns brown in air. $FeCl_3$ gives a brownish-red colour. Bleaching powder gives a bluish-green colouration, turning brown. It combines with aniline, forming $C_7H_6(OH)_2(NH_2Ph)_2$, which crystallises in small white plates [85°], sol. water (Hebebrand, *B.* 15, 1974). With *p*-toluidine it forms in like manner $C_7H_6(OH)_2(C_7H_7NH_2)_2$, crystallising in pearly plates [90°].

Di-acetyl derivative $C_7H_6(OAc)_2$. [52°].

Mono-methyl ether $C_7H_6(OH)(OMe)$. [72°]. (240°–245°). Formed, together with the di-methyl ether, by heating hydrotoluquinone (12 pts.) with NaOH (8 pts.), MeI (30 pts.) and MeOH (100 pts.) at 100°. Plates. Sol. NaOHAq.

Di-methyl ether $C_7H_6(OMe)_2$. [15°]. (214°–218°). Differs from the preceding ether in being volatile with steam and insol. alkalis. Oxidised by chromic acid to a compound $C_{16}H_{16}O_4$, crystallising from alcohol in thin, almost black, needles [153°], which may be reduced by aqueous ammonium sulphide to $C_{16}H_{18}O_4$, which separates from benzene in slender needles [173°]. The compound $C_{16}H_{18}O_4$ is converted by heating with conc. HClAq at 100° into MeCl and $C_{14}H_{12}O_4$ [232°], which separates from alcohol in plates (containing aq).

Isohydrotoluquinone $C_7H_8O_2$. [204°]. Formed by allowing toluquinone (2 pts.) to stand for 24 hours with a mixture of H_2SO_4 (5 pts.) and water (5 pts.) and reducing the resulting isotoluquinone with SO_2 (Spica, *G.* 12, 225). Pearly needles, sol. benzene, v. e. sol. alcohol and ether. Reoxidised by moist air to isotoluquinone. As only one toluquinone is indicated by theory, this body is perhaps a polymeride thereof.

HYDROXAMIC ACIDS *v.* Hydroxylamine derivatives.

HYDROXIDES. Compounds of an element or radicle with oxygen and hydrogen, not with water. The term is restricted by some chemists to compounds whose reactions indicate the presence of the group OH (*v.* Hydrates). If an hydroxide is defined to be a compound of an element or radicle with the group OH, a classification of hydroxides may be made, on the basis of composition, into mono-, di-, . . . *n*-hydroxyl compounds. Hydroxides vary much in properties; some are alkaline, *e.g.* KOH and NaOH; some are acids, *e.g.* $NO_2.OH$ and $SO_2(OH)_2$; some are neutral, *e.g.* H.OH (*cf.* Hydrates).

M. M. P. M.

HYDROXONIC ACID $C_8H_{10}N_6O_7$. An acid produced by the action of sodium-amalgam on acid potassium allantoxanate $C_4H_2N_3O_4K$ (Ponomaroff, *J. R.* 11, 56). Heavy crystalline powder, sl. sol. boiling water. Not affected by boiling HClAq or HNO_3. HClAq at 150° forms CO_2, ammonia, and a little CO. Boiling bromine water gives biuret, CO, and CO_2. Alkaline $KMnO_4$ oxidises it to allantoxanic acid. —$(NH_4)_2$A″: small needles, sl. sol. cold water.—K_2A″: small prisms. S. 1·5.—Na_2A″.—BaA″2aq;

crystalline pp. — $MgA''4aq$. — $PbA''1\frac{1}{2}aq$. — $Ag_2A''3aq$: crystalline pp.

HYDROXY- COMPOUNDS *v.* OXY- COMPOUNDS.

HYDROXYL. The radicle OH. This group occurs in alcohols and in most acids. Its presence in organic compounds is shown by the following reactions: 1. *Sodium* gives off hydrogen. — 2. *Zinc ethyl* gives off ethane (Japp, *C. J.* 37, 665).—3. PCl_5 gives off HCl.—4. AcCl and BzCl react, giving off HCl, and forming acetyl and benzoyl derivatives of the substance. 5. Ac_2O and Bz_2O also form acetyl and benzoyl derivatives. The number of hydroxyls present may be determined by saponifying the acetyl derivative with standard alkali, and titrating the product with standard acid (Schiff, *B.* 12, 1532). Jackson a. Rolfe (*Am.* **9**, 82) prefer to prepare the *p*-bromo-benzoyl derivative by means of *p*-bromo-benzoyl chloride or anhydride, and then to determine by analysis the percentage of bromine in the product.—6. According to Landwehr (*B.* 19, 2726) if a substance is added in excess to 15 c.c. of a very dilute solution of ferric chloride (prepared by adding 2 drops of a 10 p.c. solution of $FeCl_3$ to 60 c.c. of water), the production of a sulphur-yellow colour denotes the presence of hydroxyl.

Hydrogen dioxide has sometimes been termed hydroxyl.

HYDROXYLAMINE NH_2OH. (*Oxyammonia*). This base was prepared by Lossen in 1865 by reducing $C_2H_5NO_3$ by the action of Sn and HClAq. It is a product of the reduction of nitroparaffins and nitrolic acids, of HNO_3, HNO_2, some nitrates and nitrites, and is also produced by the union of H with NO. NH_2OH has not been isolated; it is known only in aqueous solution.

Formation.—1. By the partial reduction of HNO_3, by Sn and certain other metals with HClAq or H_2SO_4Aq, or by an acidified solution of $SnCl_2$. Divers (*C. J.* 43, 443) and Divers a. Shimidzu (*C. J.* 47, 597) have examined the reaction of Sn, Zn, and some other metals on HNO_3Aq in presence of HCl or H_2SO_4. They conclude that NH_2OH is a product of the interaction of both acids and the metal, and that it is not produced by the reducing action, on the HNO_3, of hydrogen formed by the reaction between the metal and the HCl or H_2SO_4 present. NH_3 is formed along with NH_2OH; according to D. a. S. the NH_3 is a product of the reaction between the metal and HNO_3. Von Dumreicher (*M.* 1, 724) found that $SnCl_2$ in presence of HCl reduces HNO_3 to NH_2OH; Divers a. Haga (*C. J.* 47, 623) find that if sufficient water is present to prevent any reaction between the HCl and HNO_3 no NH_2OH is produced; the $SnCl_2$ thus appears to react with a product of the interaction of the two acids.—2. By reducing NH_4NO_3 by Sn and HClAq (Maumené, *C. R.* 70, 147); or $NaNO_3$ by the same reagents (Donath, *W. A. B.* [2nd part] 75, 566).—3. By reducing NO by passing it into Sn and HClAq, or by reaction with $SnCl_2$ and HClAq (Von Dumreicher, *M.* 1, 724; Divers a. Haga, *C. J.* 47, 623). According to D. a. H. there is no action between NO and acidified $SnCl_2$ solution at 100°.—4. By the action of Sn and HCl, or $SnCl_2$ in HClAq, on $C_2H_5NO_2$ (Lossen, *Z.* [2] 1, 551).—5. By reducing various nitroparaffins by Sn and HCl (Meyer a. Locher, *B.* 8, 215); also by reaction of nitroparaffins with H_2SO_4 (Preibisch, *J. pr.* [2] 7, 480; 8, 316; M. a. L. *l.c.*).—6. By reducing nitrites of K or Na, and some other nitrites by H_2S (Divers, *C. J.* 43, 454; 51, 48).—7. By reaction of conc. HClAq with fulminates (*v.* p. **317**, *Reactions* 10 and 11).

Preparation.—1. A mixture of 120 grams $C_2H_5NO_3$, 400 grams granulated tin, and 800–1,000 c.c. HClAq S.G. 1·19, to which are added about 2,500–3,000 c.c. water, is placed in several large flasks; action proceeds without heating; the flasks are shaken from time to time; when the action ceases the contents of the flasks are mixed, at least an equal volume of water is added, and the Sn is ppd. by passing in H_2S; the filtrate from SnS is concentrated, at first over a flame, then on the water-bath; NH_4Cl separates out, then a compound of NH_4Cl with $SnCl_2$; these crystals are removed, and the mother-liquor is evaporated to a small bulk, when crystals of $NH_2OH.HCl$ mixed with NH_4Cl separate (the mother-liquor contains various compounds of C, and chlorides of Fe, &c., derived from the HCl or the Sn used). The crystals are shaken with a very little cold absolute alcohol, the liquid is poured off; a few drops more absolute alcohol are added, and again poured off; the crystals are now kept in contact with boiling absolute alcohol until they are dissolved, the liquid is filtered hot, and (while still hot) enough $PtCl_4$ in alcohol is added to ppt. the NH_4Cl as $2NH_4Cl.PtCl_4$; the filtered liquid yields crystals of pure $NH_2OH.HCl$ on cooling; by evaporating the mother-liquid a further yield of crystals is obtained; these should be recrystallised from hot absolute alcohol. About 47 grams $NH_2.OH$ are obtainable by this process from 120 grams $C_2H_5NO_3$ (Lossen, *A. Suppl.* 6, 220). To prepare the $C_2H_5NO_3$ for making NH_2OH, 400 grams HNO_3Aq S.G. 1·4, which have been boiled for a few minutes with about 7 grams urea nitrate and allowed to cool, are mixed with 300 grams commercial absolute alcohol; 500 grams urea nitrate are added, and the whole is distilled from a tubulated retort until from $\frac{1}{2}$ to $\frac{2}{3}$ have distilled over, when a funnel with glass stopcock is placed in the tubulus of the retort, and a freshly prepared mixture of 400 g. HNO_3Aq with 300 g. alcohol is allowed to flow into the retort, drop by drop, while distillation proceeds. The $C_2H_5NO_3$ thus obtained is washed with water, and then used as already described.—2. Von Dumreicher (*Sitz. W.* 82, 560) recommends the reduction of $C_2H_5.NO_3$ by a solution of $SnCl_2$ in HClAq; about 90 p.c. of the theoretical yield of $NH_2.OH$ is thus obtained. $C_2H_5NO_3$ is mixed with a solution of $SnCl_2$ in conc. HClAq in the ratio shown by the equation

$$C_2H_5NO_3 + 3SnCl_2 + 6HCl$$
$$= NH_2.OH + C_2H_6O + 3SnCl_4 + H_2O;$$

alcohol is added so as to make a homogeneous liquid, and after a little the whole is gently warmed until a little of the liquid gives a clear yellow pp. with H_2S. The Sn is removed by ppn. with H_2S, the filtrate is evaporated and treated as directed in 1. Instead of the tedious process of ppg. Sn by H_2S, and the long-continued evaporation of the filtrate, V. Meyer (*B.* 15, 2789) recommends to concentrate the liquid considerably, and when cold to add excess of Na_2CO_3, to filter from the pp. which contains Sn, and also Fe, Ca, &c., present as impurities, to carefully acidify with HCl, and evaporate on the water-bath; by treating the residue with hot absolute alcohol, filtering from NaCl and NH_4Cl, and cooling, crystals of $NH_2OH.HCl$ containing only about 10 p.c. NH_4Cl are obtained. These crystals are sufficiently pure for most purposes for which NH_2OH is used.—3. Ludwig a. Hein (*B.* 2, 671) pass NO (made from HNO_3, H_2SO_4, and $FeSO_4$, and stored in a gasholder) through a series of bottles containing Sn and conc. HClAq to which a little $PtCl_4$ has been added; the dissolved Sn is removed by ppn. as SnS; the rest of the process is as described in 1. In this reaction some N is always produced, but N_2O is not formed (Divers a. Hager, *C. J.* 47, 623). If air is excluded no NH_3 is produced according to D. a. H.; but Von Dumreicher (*M.* 1, 724) says that NH_3 is formed by reduction of NH_2OH by the $SnCl_2$. 4. NH_2OH is not economically prepared by the reduction of HNO_3. In one case, however, Divers obtained fully 80 p.c. of the HNO_3 as NH_2OH (*C. J.* 43, 445); in this experiment 58 c.c. conc. HClAq were mixed with 5 c.c. HNO_3Aq S.G. 1·42, and the mixture was at once poured on to 35 g. granulated tin in an atmosphere of CO_2, the flask being placed in cold water. If this method is employed the liquid must be kept very decidedly acid throughout the reaction; about 5–6 g. H_2SO_4 (supposing that acid to be used) should be present in every 100 c.c. liquid, the amount of HNO_3 in 100 c.c. not exceeding ·7 g. (Divers a. Shimidzu, *C. J.* 47, 597). Divers (*C. J.* 43, 458) has examined the action of various metals on a mixture of HNO_3 and HCl or H_2SO_4.

NH_2OHAq is obtained from one of the salts prepared as described, (i.) by forming the sulphate, by evaporating the other salt with an equivalent quantity of H_2SO_4, and crystallising from alcohol, and (ii.) by decomposing the sulphate in aqueous solution by an equivalent quantity of BaO_2H_2 in solution, and filtering from $BaSO_4$.

Properties.—NH_2OH has not been isolated. When NH_2OHAq is distilled NH_3 and water pass over, the distillate also contains some NH_2OH. NH_2OHAq is colourless and odourless; it has an alkaline reaction, and acts as an energetic reducer. An alcoholic solution of NH_2OH, obtained by decomposing conc. $2NH_2OH.H_2SO_4$Aq by KOH in alcohol, reddens and inflames the skin. NH_2OHAq produces pps., insol. excess, in solutions of $ZnSO_4$, $NiSO_4$, $FeCl_3$, alum, Cr-alum, and Pb acetate; pps. are not produced from salts of Mg, Ca, Sr, Ba. NH_2OHAq is unstable, it is decomposed by KOHAq. NH_2OHAq is distinctly basic; in its reactions with acids it resembles NH_3Aq, both combine with the acids to form salts M.HCl, $M_2.H_2SO_4$, &c., when M = NH_2OH or NH_3. The heat of neutralisation of NH_2OHAq is considerably less than that of NH_3Aq; Thomsen (*Th.* 1, 405) gives these numbers: $[2NH^2OHAq,2HClAq] = 18{,}520$; $[2NH^2OHAq,H^2SO^4Aq] = 21{,}580$; the values for NH_3 are 24,540 and 28,150 respectively. The introduction of the acidic group OH in place of H considerably decreases the basic character of the molecule. More heat is produced in the formation, from the elements, of an aqueous solution of NH_2OH than of NH_3; Thomsen's numbers are $[N,H^3,O,Aq] = 24{,}290$; $[N,H^3,Aq] = 20{,}320$; similarly with the hydrochlorides $[N,H^4,O,Cl] = 76{,}510$; $[N,H^4,Cl] = 75{,}790$ (*Th.* 2, 84).

As $NH_2.OH$ cannot be gasified its molecular weight is unknown. Lossen has shown that there are three isomerides of the form NRR.OR, and three of the form $NR_IR_I.OR$, where R is one monovalent radicle and R_I is another monovalent radicle. It appears then as if each H in NH_2OH were differently related to the rest of the molecule from the other H atom: the formula $NH_2.OH$, however, shows two H atoms similarly related to the rest of the molecule. This formula is confirmed by the production of hydroxylamine by reducing nitrites ($NO_2.OH$), and by the general reactions and combinations of the body. If the molecule of hydroxylamine is represented by the formula $HO.H_2N—NH_2.OH$, the existence of all the observed isomeric derivatives is accounted for (*v.* HYDROXYLAMINE DERIVATIVES).

Detection and Estimation.—Traces of salts of NH_2OH ppt. Cu_2O from fairly conc. KOHAq or NaOHAq to which a little $CuSO_4$Aq has been added (Lossen) $[2NH_3O + 4CuO = N_2O + 2Cu_2O + 3H_2O]$. NH_2OH may be estimated by titration with standard I, in presence of MgO added to neutralise HI $[2NH_3O + 2I_2 = N_2O + H_2O + 4HI]$; or by warming with solution of $Fe_2(SO_4)_3$ to 80°–90°, and determining the ferrous iron by standard $KMnO_4$Aq

$$[2Fe_2(SO_4)_3 + 2NH_3O = 4FeSO_4 + 2H_2SO_4 + N_2O + H_2O]$$

(*v.* Meyeringh, *B.* 10, 1940).

Reactions.—1. NH_2OHAq reduces many *metallic salts* in solution; $CuSO_4$Aq gives a grass-green pp., becoming reddish, on boiling Cu_2O ppts.; the pp. in the cold is sol. in excess of NH_2OHAq, access of air to the solution causes a brown-green pp. sol. on gently warming; ammoniacal $CuSO_4$Aq is decolourised by NH_2OHAq, $CuSO_4$ with excess of KOH is reduced to Cu_2O; $HgCl_2$Aq is reduced to HgCl; $AgNO_3$ gives Ag with evolution of gas (N_2O and N); salts of Au and Pt are reduced to metal, the latter on warming (Fremy, *C. R.* 70, 61, 1207; Lossen, *B.* 8, 357); K_2CrO_4Aq is reduced, but only on warming, addition of a little H_2SO_4 causes rapid evolution of gas and formation of a brown pp. (Lossen, *A. Suppl.* 6, 235). In these reactions the NH_2OH is generally completely decomposed to H_2O, N_2O, and N; according to Meyeringh (*B.* 10, 1940) and Donath (*W. A. B.* 75 [2nd part], 566), only N_2O is evolved.—2. According to Von Dumreicher (*M.* 1, 724) *acidified stannous chloride* reduces NH_2OH to NH_3 at 100°; but Divers a. Haga (*C. J.* 47, 623) assert that no NH_3 is produced if access of air is prevented.—3. *Tin and hydrochloric acid* slowly reduce NH_2OH to NH_3 (Lossen); according to Divers a. Haga (*l.c.*) Sn and hot conc. HClAq have hardly any action on $NH_2OH.HCl$; Divers a. Shimidzu (*C. J.* 47, 597) say that Zn and H_2SO_4Aq likewise have practically no action on $2NH_2OH.H_2SO_4$.—4. NH_2OHAq and salts of NH_2OH are decomposed by *potash* with evolution of N, NH_3, and a little N_2O.—5. *Iodine* quickly decomposes NH_2OH and its salts to N_2O and H_2O with formation of HI.—6. *Ferric sulphate* is reduced by NH_2OH and its salts to $FeSO_4$, with evolution of N_2O.—7. Contact with *zinc*, in absence of acid, decomposes NH_2OH and its salts (Divers a. Shimidzu, *C. J.* 47, 597).—8. *Sodium nitrate* causes evolution of N_2O from $2NH_2OH.H_2SO_4Aq$; dilute solutions of KNO_2 and $2NH_2OH.H_2SO_4$ only react when boiled (V. Meyer, *C. C.* 1876. 620).

Combinations.—NH_2OHAq combines with many *acids* to form salts. In these reactions NH_2OH behaves similarly to NH_3; the acid and base combine, and the salt is the only product of the interaction. The salts of NH_2OH have the composition BA_I B_2A_{II} B_3A_{III}, where $B = NH_2OH$, A_I = monobasic acid, A_{II} = dibasic acid, A_{III} = tribasic acid. The salts of NH_2OH crystallise without water; they are easily decomposed by heat, generally with evolution of N and N_2O. The chief salts are *acetate* $NH_2OH.C_2H_4O_2$, crystallises from warm absolute alcohol; *hydrochloride* $NH_2OH.HCl$, crystallises from alcohol or water, melts at 100°, and then decomposes violently to N, HCl, H_2O, and NH_4Cl. V. Meyer (*B.* 15, 2789) says that the presence of 10–15 p.c. NH_4Cl in $NH_2OH.HCl$ is not objectionable for most purposes for which the salt is used, and that the salt is perfectly stable when it is mixed with some NH_4Cl. If, however, it should contain any HCl or $FeCl_3$ the whole of the $NH_2OH.HCl$ is slowly changed to NH_4Cl. *Nitrate* $NH_2OH.HNO_3$, easily sol. in absolute alcohol; *phosphate*, $NH_2OH.H_3PO_4$, separates in small crystals on mixing dilute solutions of Na_2HPO_4, and an easily sol. salt of NH_2OH; *sulphate* $2NH_2OH.H_2SO_4$, very sol. in water, ppd. by alcohol. Meyeringh (*B.* 10, 1946) describes some double salts: *hydroxylamine alum* $(2NH_2OH.H_2SO_4).Al_2(SO_4)_3.24H_2O$, and a *chrome-alum* $(2NH_2OH.H_2SO_4).Cr_2(SO_4)_3.24H_2O$, and *iron alum* $(2NH_2OH.H_2SO_4).Fe_2(SO_4)_3.24H_2O$. These double salts are formed in octahedral crystals by mixing conc. solutions of their constituent salts and allowing to crystallise; the double salt $(2NH_2OH.H_2SO_4).MgSO_4.6H_2O$ was obtained by mixing solutions of the constituent salts.

M. M. P. M.

HYDROXYLAMINE DERIVATIVES. Hydroxylamine is a very important reagent in organic chemistry, since it reacts with aldehydes and ketones with elimination of water, forming the oxims (V. Meyer a. Janny, *B.* 15, 2783; 16, 167)

$$R.CHO + H_2NOH = RCNOH + H_2O$$
$$R.CO.R' + H_2NOH = RR'CNOH + H_2O.$$

The oxims are also called isonitroso- compounds, and are frequently interchangeable with nitroso-compounds. Thus, nitroso-phenol is identical with the mono-oxim of quinone; and the oxim of pyruvic acid is identical with β-nitroso-propionic acid. The reaction of hydroxylamine on ketones sometimes does not take place when there are no hydrogen atoms attached to the carbon united with the carbonyl (Herzig a. Zeisel, *B.* 21, 3493).

Thioaldehydes react upon hydroxylamine in the same manner as aldehydes, producing the same compounds.

Alkoyl derivatives of hydroxylamine

Benzoyl derivative BzNH.OH. *Benzhydroxamic acid.* [125°]. S. 2·2 at 6°. If hydroxylamine hydrochloride (1 pt.) be dissolved in water (9 pts.) and the solution, after neutralisation with NaOH, be mixed with benzoyl chloride (3 pts.) in the cold, di-benzoyl-hydroxylamine separates while the benzoyl hydroxylamine which remains in solution may be ppd. as Ba salt by baryta, and then liberated by H_2SO_4 (Lossen, *A.* 161, 347). Trimetric plates (from alcohol); $a:b:c = \cdot356:1:\cdot022$ (Klein, *A.* 166, 180). M. sol. water, v. e. sol. alcohol, sl. sol. ether and CS_2, insol. benzene. Decomposed somewhat violently by heat. Acid in reaction. Boiling dilute HCl or H_2SO_4 split it up into hydroxylamine and benzoic acid.

Salts. — BzNH.OK(BzNH.OH): trimetric prisms or plates, m. sol. warm water, sl. sol. alcohol. Crystallises from an alcoholic solution even in presence of excess of caustic potash (BzNH.ONa)(BzNH.OH) 3aq: plates. Effloresces in dry air. Its aqueous solution gives white pps. with solutions of $CaSO_4$, alum, $MnCl_2$, and lead nitrate; a nearly white pp. with $CuSO_4$; a green pp. with chrome alum; a whitish-green pp. with $NiSO_4$; a peach-coloured pp. with cobalt nitrate; and a yellow pp. with mercuric chloride. All these pps. dissolve in excess. Silver nitrate gives a white pp., insol. excess, and rapidly blackening. $FeCl_3$ gives a dark-red pp. dissolving in excess with formation of an intense red solution. This characteristic colouration is destroyed by conc. HClAq but reappears on dilution.—$Ba(O.NHBz)_2$: minute needles, formed by neutralising the acid potassium salt with ammonia and ppg. with barium chloride. —$Ba(ONHBz)_2(HONHBz)_2$: crystallises in small prisms, together with free benzoyl-hydroxylamine, when the neutral Ba salt is decomposed by an insufficient quantity of H_2SO_4 and the filtrate is allowed to evaporate. V. sl. sol. water and alcohol.—$Ca(ONHBz)_2$: amorphous pp.—$Zn(ONHBz)_2$: crystalline pp.

Ethyl ether *v. Ethyl-hydroxylamine* (*infra*).

Di-benzoyl derivative Bz_2NOH. *Dibenzhydroxamic acid.* [153°] (Steiner, *A.* 178, 226; *cf.* Heintz, *Z.* [2] 5, 733). Formed by the action of BzCl on hydroxylamine or on benzoyl-hydroxylamine (Lossen). Formed also by treating nitro-ethane with BzCl and extracting the product with boiling benzene (Kessel, *Bl.* [2] 38, 171). Needles or prisms. Sl. sol. water, cold alcohol, ether, and CS_2, m. sol. hot alcohol, almost insol. benzene. Acid to litmus. Decomposes violently when heated above its melting-point, forming benzanilide phenyl cyanate, HOBz, and CO_2 (Pieschel, *A.* 175, 305). Boiling dilute acids split it up into hydroxylamine and benzoic acid. Boiling baryta-water forms benzoic acid and benzoyl-hydroxylamine. $FeCl_3$ does not colour solutions of di-benzoyl-hydroxylamine, but in neutral solutions it gives a reddish-yellow pp. A solution of the K salt gives white pps. with nitrate of Pb, Ag, and Co, with $MnCl_2$, with $ZnSO_4$ and with $CdSO_4$; a bluish-green pp. with chrome alum; and an apple-green pp. with $NiSO_4$. Unlike mono-benzoyl-hydroxylamine it gives no pp. with salts of the alkaline earths.—Bz_2NOK: thin pearly plates (from alcohol) or minute six-sided tables; decomposed by hot water into potassium benzoate, di-phenyl-urea, and CO_2; and by NaOH into benzoyl-hydroxylamine and NaOBz.—Bz_2NONa.—$(Bz_2NO)_2Pb$.—Bz_2NOAg.

Tri-benzoyl derivative Bz_2NOBz. Found among the products of the action of benzoyl chloride dissolved in toluene on dry hydroxylamine hydrochloride. It is also formed by heating Bz_2NOK with BzCl at 100°, afterwards removing excess of BzCl with ether, and KCl with water, and crystallising the residue from alcohol (Lossen, *A.* 161, 360; 175, 282, 299; 186, 3, 34; Steiner, *A.* 178, 225). It occurs in three modifications, and is best prepared by drenching 10 pts. of silver di-benzoyl-hydroxylamine with 30 pts. of dry benzene and adding 4 pts. of benzoyl chloride diluted with 8 pts. of benzene. The mixture gradually separates into a pp. and a liquid; the pp. is washed with ether which takes up chiefly the (α)-modification, and then with boiling alcohol which dissolves the (β)-and (γ)-modifications, together with di-benzoyl-hydroxylamine. The alcoholic solution, treated with a solution of Na_2CO_3, yields a pp. consisting of the (β)- and (γ)-modifications, which may be purified by recrystallisation from ether or alcohol, when the many-faced prisms or needles of the (β)-compound must be separated by hand-picking from the short thick rhombohedra of the (γ)-isomeride. All three modifications are split up by dry distillation into phenyl cyanate and benzoic anhydride; and are converted by alcoholic KOH into KOBz and the di-benzoyl derivative.

(α)-**Tri-benzoyl-hydroxylamine** [100°]. Monoclinic crystals; $a{:}b{:}c = 1{\cdot}856{:}1{:}1{\cdot}142$; $\beta = 81° 42'$ (Lehmann, *Z. K.* 1, 627; Klein a. Trechmann, *A.* 186, 76; *Z. K.* 1, 637). V. e. sol. ether and boiling alcohol, v. sol. boiling benzene. Boiling HClAq (S.G. 1·05) in one hour completely splits it up into benzoic acid and di-benzoyl-hydroxylamine.

(β)-**Tri-benzoyl-hydroxylamine** [142°]. Monoclinic crystals; $a{:}b{:}c = {\cdot}897{:}1{:}{\cdot}300$; $\beta = 83° 21'$. Less sol. benzene than the preceding. Insol. ether, m. sol. boiling alcohol. Not affected by boiling dilute HClAq; but at 150° it is split up by conc. HClAq into HOBz, hydroxylamine, and Bz_2NOH. Unlike the (α)-isomeride it dissolves in aqueous Na_2CO_3.

(γ)-**Tri-benzoyl-hydroxylamine** [112°]. Short monoclinic prisms; $a{:}b{:}c = {\cdot}926{:}1{:}?$; $\beta = 65° 55'$. Converted by hot dilute HClAq into the (β)-isomeride. Alcoholic KOH forms EtOBz and Bz_2NOEt.

Anisyl derivative $C_6H_4(OMe).NH.OH$. *p-Methoxy-benzoyl derivative.* [157°]. When anisyl chloride is added to a solution of hydroxylamine hydrochloride in ten times its weight of water, together with enough Na_2CO_3 to make the liquid alkaline, there separates anisic acid, anisyl-hydroxylamine, and di-anisyl-hydroxylamine. The pp. is boiled several times with water, when anisic acid and anisyl-hydroxylamine are dissolved, and may subsequently be separated by their barium salts, that of the latter being insoluble. The di-anisyl derivative which remains undissolved in the boiling water is freed from anisic acid by cold aqueous Na_2CO_3 (Lossen, *A.* 175, 284). Laminæ, v. sol. alcohol and boiling water, sl. sol. cold water, v. sl. sol. ether, insol. benzene. $FeCl_3$ colours its solution deep violet. — $C_6H_4(OMe)NHOK,C_6H_4(OMe)NH.OH$: long flat needles, moderately soluble in cold water. — $C_6H_4(OMe)NH.O.PbOAc$: pulverulent pp. (Hodges, *A.* 182, 218).

Di-anisyl derivative
$(C_6H_4(OMe)CO)_2NOH$ or
$C_6H_4(OMe).CONH\ O.C_6H_4(OMe).CO$. [143°]. Needles, v. sl. sol. ether, insol. benzene. Split up by boiling baryta-water into anisic acid and anisyl-hydroxylamine.

Benzoyl-anisyl derivative
$BzNH.O.CO.C_6H_4.OMe$. [132°]. Formed by treating benzoyl-hydroxylamine with anisyl chloride. Needles or prisms (from alcohol). Split up by heating with baryta-water into anisic acid and benzoyl-hydroxylamine. The potassium salt is split up by boiling water into anisic acid, s-di-phenyl-urea, and CO_2. Benzoyl-anisyl-hydroxylamine is resolved by distillation into anisic acid and anisyl-anilide.

Anisyl-benzoyl derivative
$C_6H_4(OMe).CO.NH.OBz$. [148°]. Formed by treating anisyl-hydroxylamine with benzoyl chloride. Needles or prisms. Split up by heating with baryta-water into benzoic acid and anisyl-hydroxylamine. The potassium salt is split up by boiling with water into benzoic acid, s-di-*p*-methoxy-di-phenyl-urea, and CO_2. Anisyl-benzoyl-hydroxylamine is split up by distillation into benzoic acid, benzoyl-anisidine, CO_2, and methoxyphenyl cyanate.

Benzoyl-anisyl-benzoyl derivative
$BzN(CO.C_6H_4.OMe).OBz$? Formed, in three modifications, by the action of BzCl on the silver salt of benzoyl-anisyl-hydroxylamine. In one preparation 35 pts. of (α), 6 pts. of (β), and 5 pts. of the (γ) variety were got.

(α)-**Modification** [114°]. Short triclinic prisms. This is the modification formed in largest quantity. When heated with dilute HCl it is split up into benzoic acid and benzoyl-anisyl-hydroxylamine; while conc. HClAq gives hydroxylamine, benzoic acid, and anisic acid. Alcoholic KOH forms benzoic ether and benzoyl-anisyl-hydroxylamine; aqueous KOH forms chiefly benzoic acid and benzoyl-anisyl-hydroxylamine, but produces also a small quantity of anisic acid and di-benzoyl-hydroxylamine. On dry distillation the (α)-modification is decomposed with slight carbonisation into phenyl cyanate and benzoyl-anisic anhydride, a small quantity of *p*-methoxy-phenyl cyanate and Bz_2O being also produced.

(β)-**Modification** [125°]. Trimetric prisms; chiefly found in the alcoholic mother-liquor of the first crystallisation of the crude product of the action of BzCl on benzoyl-anisyl-hydroxylamine. Not affected by boiling for one hour with 9 pts. of dilute HClAq (S.G. 1·05); fuming HClAq converts it into benzoic acid, anisic acid, and hydroxylamine, a little benzoyl-anisyl-hydroxylamine being likewise formed. Alcoholic KOH converts it into EtOBz and benzoyl-anisyl-hydroxylamine.

(γ)-**Modification** [110°]? Monoclinic tables; separated from the crystals of the (α)-variety by hand-picking. After fusion it takes a long time to solidify, and then melts at 120°, having perhaps been converted into the (β)-modification. Boiling dilute HCl (S.G. 1·05) forms benzoic acid, benzoyl-anisyl-hydroxylamine, and a quantity (40 p.c.) of the (β)-modification of benzoyl-anisyl-benzoyl-hydroxylamine.

Di-benzoyl-anisyl derivative $Bz_2N.O.CO.C_6H_4.OMe$. Formed, in two modifications, by the action of anisyl chloride on dibenzoyl-hydroxylamine (Lossen, *A.* 186, 21).

(α)-Modification [110°]. Monoclinic needles or prisms. Boiling dilute HCl (S.G. 1·05) easily splits it up into anisic acid and dibenzoyl-hydroxylamine. Alcoholic KOH gives, on the contrary, benzoic acid and benzoyl-anisyl-hydroxylamine. Split up by heat into phenyl cyanate and benzoic anisic anhydride, together with smaller quantities of *p*-methoxy-phenyl cyanate and Bz_2O.

(β)-Modification [110°]. Rosettes of small crystals, occurring in the last crop of crystals of its (α)-isomeride. It is scarcely attacked by boiling dilute HCl (S.G. 1·05); while prolonged heating with acid of S.G. 1·14 forms dibenzoyl-hydroxylamine, most of the substance being, however, converted into hydroxylamine, benzoic acid and anisic acid.

Anisyl-di-benzoyl derivative $MeO.C_6H_4.CO.NBz.OBz$? Two modifications of this body are formed by the action of benzoyl chloride on silver anisyl-benzoyl-hydroxylamine (Lossen, *A.* 186, 25).

(α)-Modification [137°]. Monoclinic tables. Slowly decomposed by dilute HCl (S.G. 1·05), more readily by stronger HCl (S.G. 1·14), into benzoic acid and anisyl-benzoyl-hydroxylamine. Alcoholic KOH also gives benzoic acid and anisyl-benzoyl-hydroxylamine. When heated alone it yields *p*-methoxy-phenyl cyanate and Bz_2O, together with small quantities of phenyl cyanate and benzo-anisic anhydride.

(β)-Modification [110°]. Small rosettes. Not decomposed by HCl of S.G. 1·05, and only partially attacked by acid of S.G. 1·14. Alcoholic KOH forms anisyl-benzoyl-hydroxylamine.

Anisyl-benzoyl-anisyl derivative $C_6H_4(OMe).CO.NBz.O.CO.C_6H_4(OMe)$. Formed, in two modifications, by the action of anisyl chloride on the silver salt of anisyl-benzoyl-hydroxylamine.

(α)-Modification [153°]. Very small monoclinic tables (from ether); $a:b:c = {\cdot}866:1:{\cdot}380$; $\beta = 75° \ 22'$. Dilute HCl (S.G. 1·05) easily decomposes it, forming anisic acid and anisyl-benzoyl-hydroxylamine. Alcoholic KOH forms, on the contrary, benzoic acid and di-anisyl-hydroxylamine.

(β)-Modification [149°]. Only 1 pt. of this modification is formed to 34 pts. of the preceding. It crystallises in monoclinic tables; $a:b:c = 1{\cdot}002:1:{\cdot}789$; $\beta = 89° \ 51'$.

Di-anisyl-benzoyl derivative $(C_6H_4(OMe).CO)_2NOBz$? [148°]. Formed, in only one modification, by the action of BzCl on silver di-anisyl-hydroxylamine. Monoclinic crystals. Slowly attacked by HCl of S.G. 1·05, more rapidly by stronger acid, forming benzoic acid and di-anisyl-hydroxylamine only. Alcoholic KOH reacts in like manner, but forms also a little anisic acid and anisyl-benzoyl-hydroxylamine.

Benzoyl-di-anisyl derivative $BzN(CO.C_6H_4.OMe).OBz$? Formed, in two modifications, from the silver derivative of benzoyl-anisyl-hydroxylamine and anisyl chloride.

(α)-Modification [138°]. Triclinic prisms; $a:b:c = {\cdot}803:1:{\cdot}[illegible]55$; $\alpha = 99° \ 45'$; $\beta = 115° \ 58'$; $\gamma = 74° \ 43'$. Easily decomposed by HCl of S.G. 1·05 into anisic acid and benzoyl-anisyl-hydroxylamine. Alcoholic KOH acts in like manner.

(β)-Modification [138°]. Triclinic tables; $a:b:c = {\cdot}428:1:1{\cdot}400$; $\alpha = 103° \ 7'$; $\beta = 96° \ 16'$; $\gamma = 89° \ 25'$. Behaves like the (α)-modification when treated with HCl or KOH.

Cinnamoyl derivative $C_6H_5.CH:CH.CO.NH.OH$. [110°]. Formed, together with the di-cinnamoyl derivative and cinnamic acid, by the action of cinnamoyl chloride on hydroxylamine in aqueous solution (Rostoski, *A.* 178, 213). Crystalline; sl. sol. cold, m. sol. hot, water; v. sol. alcohol and ether, insoluble in benzene. Ferric chloride colours its solution deep violet.—$(C_6H_5.CH:CH.CO.NH.O)_2HK$: very easily decomposable yellow crystals.—$(C_6H_5.CH:CH.CO.NH.O)_2HNa$: yellow plates.—$(C_9H_7O.NH.O)_2Ba$: sparingly soluble yellow crystalline powder which, when heated, gives off CO_2 and NH_3.—$(C_9H_7O.NHO)_2Pb$: yellowish-white pp.

Di-cinnamoyl derivative $(C_6H_5.CH:CH.CO)_2N.OH$. [152°]. Formed as above. Prisms or laminæ; sl. sol. ether, insol. water and baryta-water, v. sol. hot alcohol. Its salts when once separated from the aqueous solution are no longer soluble in water. The K salt is decomposed by boiling with water and converted for the most part into cinnamate. When the compound is heated to incipient carbonisation a resin is formed, from which small quantities of a crystalline powder $C_{17}H_{11}N_3O_4$ may be extracted.—$(C_9H_7O)_2NOK$: yellow powder.—$((C_9H_7O)_2NO)_2Pb$: amorphous yellowish pp.—$(C_9H_7O)_2NOAg$: white pp.

o-Amido-benzoyl derivative $NH_2.C_6H_4.CO.NH.OH$. [82°]. From anthranil *ν*-carboxylic acid and hydroxylamine. Glittering plates (from water) (E. von Meyer a. Bellmann, *J. pr.* [2] 33, 20).

(α)-Naphthoyl derivative $C_{10}H_7.CO.NH.OH$. [187°]. From hydroxylamine and (α)-naphthoyl chloride (Ekstrand, *B.* 20, 1353). Glistening scales, sol. boiling water, almost insol. alcohol. Its potassium salt decomposes very readily with formation of (α)-naphthylamine.

(β)-Naphthoyl derivative $C_{10}H_7.CO.NH.OH$. [168°]. From hydroxylamine (1 mol.) and (β)-naphthoyl chloride (Ekstrand, *B.* 20, 1353). Small dimetric scales, v. sol. alcohol.

Di-(α)-naphthoyl derivative $(C_{10}H_7.CO)_2N.OH$. [150°]. Formed, together with the mono-(α)-naphthoyl derivative (*v. supra*), by the action of (α)-naphthoyl chloride on hydroxylamine. Needles, sol. boiling alcohol. Its K salt crystallises in needles, sol. alcohol.

Di-(β)-naphthoyl derivative $(C_{10}H_7CO)_2NOH$. [171°]. Formed like the preceding. Small needles. Forms a crystalline potassium salt.

(αβ)-Di-naphthoyl derivative $(C_{10}H_7CO)_2NOH$. [160°]. From (β)-naphthoyl-hydroxylamine and (α)-naphthoyl chloride at 100°. Needles (from alcohol).

Phthalyl-derivative $C_6H_4:C_2O_2:NOH$. [230°]. Formed by the action of phthalyl chloride or of phthalic anhydride on hydroxylamine (Cohn, *A.* 205, 295; Lach, *B.* 16, 1781). Needles or plates (from alcohol); v. sl. sol. water, v. sol. boiling alcohol, insol. ether and benzene. KOHAq dissolves it, forming a red solution. When boiled with KOH (1 mol.) dissolved in alcohol it is split up into CO_2 and *o*-amido-benzoic acid. When boiled with a larger quantity of KOH (2 mols.) in alcohol it gives the phthaloxyl derivative—$C_6H_4{:}C_2O_2{:}NONa$: red amorphous powder.—$C_6H_4{:}C_2O_2{:}NOK$: red pp., obtained by adding caustic potash (1 mol.) to an alcoholic solution. Readily decomposed by treatment with water.—$BaCl_2 4(C_6H_4{:}C_2O_2{:}NO)_2Ba$.—$(C_6H_4C_2O_2NO)_3Pb_2(OH)$ 3aq: light-red pp.—$C_6H_4{:}C_2O_2{:}NOAg$: dark-red pp.

Phthaloxyl derivative $CO_2H.C_6H_4.CO.NH.OH$. Formed from the phthalyl derivative by warming with alcoholic KOH. Its solution is acid in reaction, and gives a violet colour with $FeCl_3$, but it quickly decomposes with separation of its anhydride, the phthalyl derivative.—$KC_8H_6NO_4$: yellowish crystals (from water); v. e. sol. cold water.—$PbC_8H_5NO_4$: white pp.

ALKYL DERIVATIVES OF HYDROXYLAMINE.

Methyl-hydroxylamine $H_2N(OMe)$. The hydrochloride forms pearly scales (148° uncor.); does not reduce alkaline solutions of copper. It is formed by boiling the methyl ether of the oxim of benzoic aldehyde with HCl (Petraczek, *B.* 16, 827).—$B'_2H_2PtCl_6$: orange-red tables or prisms (Waldstein).

Benzoyl derivative BzMeN.OH. [65°]. From di-benzoyl-methyl-hydroxylamine by warming with conc. KOHAq and passing CO_2 into the product (Lossen a Zanni, *A.* 182, 226). Rectangular tables (from ether-benzene). Decomposed by HCl into hydroxylamine and methyl benzoate.

Di-benzoyl derivative BzMeNOBz. [c. −15°]. Formed by the action of MeI on an ethereal solution of potassium di-benzoyl-hydroxylamine. Oil.

Ethylene-di-hydroxylamine.

Di-benzoyl derivative $(NBz_2O)_2C_2H_4$. [148°]. Formed by boiling silver di-benzoyl-hydroxylamine with an alcoholic solution of ethylene bromide (Eiseler, *A.* 175, 342). Prisms, sl. sol. cold ether and alcohol; moderately stable towards KOHAq.

Ethyl-hydroxylamine $NH_2.OEt$ or EtHN.OH. (68°). S.G. $\frac{7\cdot5}{}$ ·883. Formed by decomposing ethyl-benzoyl-ethyl-hydroxylamine with HCl, and liberated from its hydrochloride by conc. KOHAq (Lossen a. Zanni, *A.* 182, 223; Gürke, *A.* 205, 274). Combustible liquid, with powerful odour; miscible with water, alcohol, and ether. Alkaline in reaction. Gives a white pp. with silver nitrate, and on boiling reduction takes place with evolution of gas. When added in excess to cupric sulphate solution it forms a deep blue liquid, whence an apple-green pp. is formed on boiling, reduction not taking place. With $HgCl_2$ it gives a golden flocculent pp.—B'HCl. [128°]. Scales; obtained by heating ethyl-benzoyl-ethyl-hydroxylamine with HCl in ether. Volatile. HClAq (S.G. 1·14) at 150° decomposes it into EtCl and hydroxylamine.—$B'_2H_2PtCl_6$: prisms; v. sol. water and alcohol.—$B'H_2SO_4$: v. e. sol. water and alcohol.—$B'H_2C_2O_4$: colourless powder.

Benzoyl-ethyl-hydroxylamine NHBz.OEt. [65°]. Formed by the action of EtI on potassium benzoyl-hydroxylamine (Waldstein, *A.* 181, 385); the proportions being: benzoyl-hydroxylamine (1 mol.), conc. alcoholic KOH (2 mols.), and EtI (1 mol.); after being left for 24 hours, with frequent agitation, the solution is filtered from KI, freed from alcohol by evaporation, dissolved in water, and subjected to a stream of CO_2, and the NHBz(OEt) extracted with ether. The same compound is also formed by treating ethyl-hydroxylamine with benzoyl chloride (Gürke, *A.* 205, 278; Bertram, *A.* 217, 16); and by treating benzoic ether with hydroxylamine (Tiemann a. Krüger, *B.* 18, 740).

Properties.—Triclinic crystals (from alcohol); $a{:}b{:}c = \cdot610 : 1 : \cdot852$; $\alpha = 109° \, 31'$; $\beta = 85° \, 32'$; $\gamma = 100° \, 31'$. V. e. sol. ether and alcohol; m. sol. water. Soluble in aqueous KOH (1 mol.) forming a solution from which it is reppd. by CO_2 and by acids, and which gives pps. with salts of Ag, Hg, and Pb. Hot conc. HClAq in sealed tubes splits it up into benzoic acid and ethyl-hydroxylamine hydrochloride. By heating alone to 190° it is converted into phenyl cyanate, benzamide, aldehyde, and alcohol. PCl_5 gives benzoyl-ethoxim chloride Ph.CCl:N.OEt. (230°).—BzAgN.OEt: white pp.

Ethyl-benzoyl-hydroxylamine EtNBz.OH.

(α)-Modification [54°]. S.G. 1·208. S. (ligroïn of S.G. ·65) 1·3. Formed, together with KOBz, by heating (α)-di-benzoyl-ethyl-hydroxylamine with conc. KOHAq. Formed also, together with the (β)-isomeride, by treating benzimido-ethyl ether with conc. hydroxylamine hydrochloride (Lossen, *B.* 17, 1587). Monoclinic tables or prisms (from benzene-ether); $a{:}b{:}c = 1\cdot49 : 1 : 1\cdot53$; *inclination of optical axes* = 117°. V. sol. alcohol and ether, m. sol. water. Sol. KOHAq, forming a solution which is ppd. by metallic salts. On heating with HClAq it is resolved into hydroxylamine and benzoic ether. Decomposes at 180° into benzonitrile, BzOEt, alcohol, water, and nitrogen, with smaller quantities of benzamide, benzoic acid, and CO_2.

(β)-Modification [68°]. S.G. 1·185. S. (ligroïn of S.G. ·652) 2·21. Formed as above, and by the action of boiling KOH (1 pt.) dissolved in water (1 pt.) upon (β)-di-benzoyl-ethyl-hydroxylamine (Gürke, *A.* 205, 286), and upon ethyl-benzoyl-anisyl-hydroxylamine (Pieper, *A.* 217, 5). Monoclinic crystals; $a{:}b{:}c = 1\cdot24 : 1 : 1\cdot40$; *inclination of optical axes* = 72·5° (Tenne, *A.* 217, 5). Less soluble in alkalis than the (α)-modification. Decomposed by HCl, and by distillation, into the same products as the (α)-isomeride.

Anisyl-ethyl-hydroxylamine $(C_8H_7O_2)EtNOH$. [84°]. From ethyl-hydroxylamine and anisyl chloride (Pieper, *A.* 217, 16). Monoclinic tables (from ether). Forms with KOH a salt. Conc. HCl gives anisic acid and ethyl hydroxylamine.

Ethyl-anisyl-hydroxylamine $C_8H_7O_2NH.OEt$. [82°]. Formed by treating anisyl-benzoyl-ethyl-hydroxylamine with conc. KOHAq, and ppg. by CO_2 (Eiseler, *A.* 175, 338).

Crystals; v. e. sol. alcohol and ether. Split up by HCl into anisic ether and hydroxylamine.

Di-benzoyl-ethyl-hydroxylamine $Bz_2N.OEt$. Two, or possibly three, modifications of this compound are formed in the reaction between silver di-benzoyl-hydroxylamine and EtI; the (α)-variety is formed in the greater quantity, and crystallises out first; only 2 or 3 p.c. of the (β)-modification is formed; there is perhaps also an oily variety (Gürke, *A.* 205, 280).

(α)-**Modification** [58°]. S.G. $\frac{18\cdot4}{}$ 1·248. Trimetric crystals; *a*:*b*:*c* = ·697:1:·591. V. sol. ether and alcohol, insol. benzene. Decomposes at 180° into benzoic acid, benzonitrile, and aldehyde. Conc. KOHAq converts it into benzoic acid and (α)-ethyl-benzoyl-hydroxylamine. Conc. HClAq gives benzoic acid, benzoic ether, and hydroxylamine (Eiseler, *A.* 175, 330).

(β)-**Modification** [63°]. S.G. ^{19} 1·239. Formed as above. It is also the chief product of the action of BzCl on (α) or (β) ethyl-benzoyl-hydroxylamine. Triclinic crystals; *a*:*b*:*c* = ·556:1:·714; α = 118° 25′; β = 102° 37′; γ = 90° 52′. More soluble in alcohol and ether than the (α)-modification; insol. ligroïn. When heated it yields the same products as its isomeride, but requires a temperature of 225°. Conc. HClAq also acts upon it in the same way as upon the (α)-variety. KOHAq acts upon it with more difficulty than upon its isomeride, and produces (β)-ethyl-benzoyl-hydroxylamine.

Benzoyl-ethyl-benzoyl hydroxylamine [49°]. From NBzEtAgO and BzCl (Lossen, *B.* 10, 2223); or from NBzEtHO, BzCl, and KOHAq (Pieper, *A.* 217, 8). Trimetric crystals, *a*:*b*:*c* = ·624:1:2·587. V. sol. alcohol or ether, insol. water or petroleum. Split up by HCl into benzoic acid and hydroxylamine.

Benzoyl-anisyl-ethyl-hydroxylamine $BzN(C_8H_7O_2).OEt$. Formed, in two modifications, by the action of EtI on silver benzoyl-anisyl-hydroxylamine (Eiseler, *A.* 175, 326; Pieper, *A.* 217, 2).

(α)-**Modification** [74°] (P.); [69°] (E.). Monoclinic tables (from ether-benzene); *a*:*b*:*c* = 1·518:1:·666. Decomposed by alcoholic KOH into potassium anisate and (α)-ethyl-benzoyl-hydroxylamine [54°]. HCl forms benzoic ether, anisic acid, and hydroxylamine.

(β)-**Modification**. Oil.

Ethyl-benzoyl-anisyl-hydroxylamine $EtNBz.OC_8H_7O_2$. [89°]. Formed by treating ethyl-benzoyl-hydroxylamine with anisyl chloride and aqueous KOH (Pieper, *A.* 217, 4). Monoclinic crystals (from ether); *a*:*b*:*c* = ·748:1:·803. With conc. KOHAq it gives (β)-ethyl-benzoyl-hydroxylamine [68°] and potassium anisate. On distillation it gives benzonitrile, anisic acid, and aldehyde.

Anisyl-benzoyl-ethyl-hydroxylamine $BzN(C_8H_7O_2).OEt$. [79°]. Formed, together with an oily isomeride, by treating silver anisyl-benzoyl-hydroxylamine with EtI (Eiseler). Triclinic prisms. Decomposed by KOH into ethyl-anisyl-hydroxylamine and KOBz. HCl gives hydroxylamine, anisic ether, and benzoic acid.

Benzoyl-ethyl-anisyl-hydroxylamine $BzNEt.OC_8H_7O_2$. [64°]. From silver benzoyl-ethyl-hydroxylamine and anisyl chloride (Pieper, *A.* 217, 10). Triclinic crystals (from ether); *a*:*b*:*c* = ·773:1:·[illegible]55. M. sol. alcohol and ether, insol. water and ligroïn. Not attacked by a solution of 2 pts. of KOH in 3 pts. of water; but a solution of equal weights of potash and water forms potassium anisate and benzoyl-ethyl-hydroxylamine [67°]. Dilute HCl at 100° forms benzoic acid, anisic acid, and ethyl-hydroxylamine; a still more dilute acid gives anisic acid and benzoyl-ethyl-hydroxylamine [67°]. On distillation it is split up into anisic ether and phenyl cyanate.

Anisyl-ethyl-benzoyl-hydroxylamine $C_8H_7O_2NEt.OBz$. [94°]. From anisyl-ethyl-hydroxylamine, BzCl, and the calculated quantity of aqueous KOH (Pieper, *A.* 217, 18). Monoclinic crystals (from ether). Sl. sol. alcohol or ether, insol. water or light petroleum. Hot conc. KOHAq gives anisyl-ethyl-hydroxylamine [84°] and benzoic acid. HCl at 100° acts similarly, the anisyl-ethyl-hydroxylamine being subsequently broken up into anisic acid and ethyl-hydroxylamine. On distillation it is decomposed, but not neatly.

Phthalyl-ethyl-hydroxylamine $C_6H_4{:}C_2O_2{:}NOEt$. [104°]. (c. 270°). From silver phthalyl-hydroxylamine and EtI (Cohn, *A.* 205, 295). Trimetric needles, sol. ether and petroleum, insol. Na_2CO_3Aq. When heated with potash it yields ethyl-amido-benzoic acid. It resembles the nitrolic acids in giving a red colouration with alkalis.

Methyl-ethyl-hydroxylamine.

Methyl-ethyl-benzoyl-hydroxylamine MeNEt.OBz. Prepared by the action of EtI on methyl-benzoyl-hydroxylamine dissolved in alcoholic KOH. Oil, with pleasant odour. Decomposed by dilute HCl into methyl benzoate and ethyl-hydroxylamine.

Benzoyl-methyl-ethyl-hydroxylamine BzNMe.OEt. From silver benzoyl-ethyl-hydroxylamine (1 mol.) and MeI (1 mol.) in ether (Waldstein, *A.* 181, 393). Oil; miscible with alcohol and ether. Decomposed by hot dilute HCl.

Ethyl-benzoyl-methyl-hydroxylamine EtNBzOMe. Formed by the action of MeI on (α)-ethyl-benzoyl-hydroxylamine dissolved in alcoholic KOH. Oil. Decomposed by HCl into methyl-hydroxylamine and benzoic ether.

Di-ethyl-hydroxylamine $NEt_2.OH$ or NEtH.OEt. Formed, together with hydroxylamine, by reducing nitric ether with tin and HCl (Lossen, *A. Suppl.* 6, 238). Its hydrochloride remains in the mother-liquor, from which hydroxylamine hydrochloride has crystallised. The free base, separated from its salts by KOH and extracted by ether, is a strongly alkaline syrup, v. sol. water, not easily volatile with steam. Its aqueous solution forms with $FeCl_3$ chrome-alum, cobalt nitrate, and lead nitrate, pps. insoluble in excess and with $CuSO_4$ a bluish-white pp., dissolving in excess to a violet-brown solution. It reduces silver oxide on heating. It also reduces boiling aqueous $HgCl_2$.

Salts.—B′HCl: syrup.—$B'_2H_2PtCl_6$: orange-red crystals (from alcohol).—$B'_2H_2SO_4$: minute laminæ; ppd. by ether from its solution in alcohol.—$B'_2H_3PO_4$: prisms (from water) or hair-like needles (from alcohol).—$B'H_2C_2O_4$: stellate groups of prisms (from water) or minute needles (from boiling alcohol).—$B'_2H_2C_2O_4$: prisms (from water); insol. alcohol.

Benzoyl derivative Et_2NOBz or EtNBz.OEt. (244° i.V.). S.G. $\frac{17}{}$ 1·026. Formed by the action of EtI on ethyl-benzoyl-hydroxylamine dissolved in alcoholic KOH. Yellowish aromatic oil; v. sol. alcohol and ether. Resolved by heating with HClAq into benzoic ether and ethyl-hydroxylamine.

Tri-ethyl-hydroxylamine NEt_2OEt. S.G. $\frac{0}{}$ ·8935. Formed by mixing $ZnEt_2$ with nitroethane and ether in an atmosphere of CO_2, and after a fortnight decomposing the product with water (Bevad, *J. R.* 20, 125). Oil; v. sl. sol. water, miscible with alcohol, ether, and benzene. Its salts are very hygroscopic, and reduce silver, cupric, and mercuric salts.—$B'_2H_2C_2O_4$.

Benzyl-hydroxylamine

(α)-modification $NH_2.OCH_2Ph$. Formed by warming the benzyl derivative of the oxim of acetone with aqueous HCl; thus:

$Me_2C{:}NOC_7H_7 + OH_2 = Me_2CO + H_2NOC_7H_7$

(Janny, *B.* 16, 175). Formed also in like manner by treating the (α)-benzyl derivative of benzaldoxim ((α)-benzylidene-benzyl-hydroxylamine) with conc. HClAq (Beckmann, *B.* 22, 515). Hydrochloride B'HCl. Soft, silvery plates, sl. sol. water, v. sl. sol. cold, v. sol. hot, alcohol. Acid in reaction. Sublimes between 230° and 260° without previous fusion. Readily condenses with benzoic aldehyde. Boiling HI converts it into iodo-benzene and NH_3. Ureide $NH_2.CO.NH.OC_7H_7$. [139°] (Behrend a. Leuchs, *B.* 22, 385).

(β)-modification $C_7H_7.NH.OH$. [58°]. Obtained from the (β)-benzyl ether of benzaldoxim by the action of conc. HClAq at a high temperature (Beckmann, *B.* 22, 514). Formed also by heating (β)-di-benzyl-hydroxylamine with conc. HClAq at 130° (Behrend a. Leuchs, *B.* 22, 615). Needles (from petroleum-ether).—B'HCl [110°]. Broad needles, v. sol. cold alcohol, v. e. sol. water. Reduces Fehling's solution in the cold.

Di-benzyl-hydroxylamine $(C_6H_5.CH_2)_2N.OH$ [123°] uncor. Prepared by heating for two hours on the water-bath a solution of 30 g. hydroxylamine hydrochloride, 60 g. Na_2CO_3 10aq and 30 g. benzyl chloride in water and sufficient alcohol to just dissolve the benzyl chloride; on cooling the product crystallises out (yield: 14 g.) (Schramm, *B.* 16, 2184; Walder, *B.* 19, 1626). It is perhaps accompanied by a more strongly basic isomeride (Behrend, *B.* 22, 385). Long white needles. V. sol. alcohol, ether, benzene, sl. sol. ligroïn, CS_2, HOAc, and hot water. Dissolves in HCl but not in NaOH or NH_3. Not decomposed by conc. HClAq at 130°. By long boiling with acetic acid saturated with HCl it is split up into benzaldehyde and benzylamine; acetyl chloride has the same effect. Boiled with alcoholic benzyl chloride it yields tri-benzyl-hydroxylamine $(Ph.CH_2)_2N.OCH_2.Ph$. By the action of PCl_3 and treatment with water di-benzyl-amine is formed, the reaction probably being:

$(C_7H_7)_2N.OH + PCl_3 = (C_7H_7)_2N.O.PCl_2 + HCl$ and $(C_7H_7)_2N.O.PCl_2 + 3H_2O$

$= (C_7H_7)_2NH + PO_4H_3 + 2HCl.$

MeI and NaOEt gives a compound $(C_7H_7)_4N_2OHI$ which appears to be the hydriodide of the anhydride $(C_7H_7)_2N.O.N(C_7H_7)_2$. Heated with ethyl iodide and alcoholic sodium ethylate it gives di-benzyl-ethyl-amine (c. 300°) and a base $C_{14}H_{21}N$ which forms felted crystals [84°]. Propyl iodide and a solution of sodium in propyl alcohol give benzyl-amine, propyl ether, and a small quantity of benzyl-benzoate. With a very dilute colourless solution of Fe_2Cl_6 it gives a yellow colour on standing. By the action of nitrous acid without cooling, di-benzyl-nitrosamine is formed; when kept cold the product is the nitrous ether $(C_6H_5.CH_2)_2N.O.NO$: [84°] which crystallises from dilute alcohol in flat white needles; v. sol. alcohol and ether, sl. sol. ligroin, insol. water (Walder, *B.* 19, 3287).

Salts.—B'HCl: pearly plates.—$B'_2H_2PtCl_6$: sparingly soluble brownish-red crystals. — B'HCl, $HgCl_2$: white plates, sol. warm alcohol, nearly insol. water.—Picrate $B'C_6H_2(NO_2)_3OH$: [151° cor.]; glistening yellow plates, v. sol. alcohol and ether, insol. water (Walder, *B.* 20, 1751).

Anhydride? $\{(C_7H_7)_2N\}_2O$. The hydroiodide (B''HI) [148°], erroneously called 'tetra-benzyl-oxy-ammonium iodide,' is formed by heating di-benzyl-hydroxylamine with methyl iodide; from this salt the base is obtained by the action of Ag_2O. Strongly alkaline colourless, very deliquescent crystals. V. e. sol. water, sl. sol. ether. Distils at a high temperature.—$B''H_2Cl_2$: pearly prisms, m. sol. water, insol. ether.—B''HI: see above.—$B''H_2I_2$: [27°]; white crystals.—$B''(HNO_3)_2$: [159°]; white flat needles, sl. sol. water.—$B''H_2SO_4$: [152°]; soluble prisms.—$B''H_2Cl_2PtCl_4$: [152°]; small yellow needles, sl. sol. hot water, insol. cold water (Walder, *B.* 19, 3289).

Acetyl derivative $(C_7H_7)_2N.OAc$. [173°]. From di-benzyl-hydroxylamine (1 mol.) and AcCl (1 mol.). Feathery crystals (from dilute alcohol); m. sol. water, v. sol. alcohol.

Benzoyl derivative $(C_7H_7)_2NOBz$. [97°]. From di-benzyl-hydroxylamine and BzCl (Behrend a. Leuchs, *B.* 22, 385). Needles (from alcohol). Converted by boiling alcoholic KOH into di-benzyl-hydroxylamine and benzoic acid.

(β)-modification $C_6H_5.CH_2NH.O.CH_2C_6H_5$. An oil, which accompanies the preceding. Conc. HClAq at 130° splits it up into benzyl chloride and the (β)-modification of benzyl-hydroxylamine (Behrend a. Leuchs, *B.* 22, 615).

Tri-benzyl-hydroxylamine

$(C_6H_5.CH_2)_2N.O.CH_2.C_6H_5$. [119°]. Formed by boiling di-benzyl-hydroxylamine for a long time with an alcoholic solution of benzyl chloride (Walder). Behrend and Leuchs (*B.* 22, 613) could only obtain by this method an oily tri-benzyl-hydroxylamine of basic character, mixed with an indifferent, probably isomeric, oil. Short white prisms, v. sol. alcohol and ether, insol. water.

Salts.—B'HCl: [172°]; white crystals, sl. sol. water, insol. ether.—$B'_2H_2Cl_2PtCl_4$: [c. 150°]; small reddish-yellow crystals, sl. sol. alcohol (Walder, *B.* 19, 1631; *cf.* Behrend, *B.* 22, 385).

Tri-benzyl-hydroxylamine

$(C_6H_5.CH_2)_2N.O.CH_2C_6H_5$. Formed, together with di-benzyl-hydroxylamine, by the action of an alcoholic solution of benzyl chloride (3 mols.) on benzyl-hydroxylamine hydrochloride in presence of Na_2CO_3. Dilute HClAq dissolves the di-benzyl-hydroxylamine, but not the tri-benzyl-hydroxylamine, since the hydrochloride of this body is decomposed by water. The tri-benzyl derivative is then extracted with ether (Behrend a. Leuchs, *B.* 22, 614). Oil. With conc. HClAq at 160° it gives di-benzyl-hydroxylamine [123°].

Salts.—B'HCl: [91°]; needles.—$B'_2H_2PtCl_6$: [157°]; prisms, v. sl. sol. cold alcohol. — Picrate: [132°]; v. sl. sol. water.

Tri-nitro-phenyl-hydroxylamine $C_6H_2(NO_2)_3NH.OH$. [100°]. Formed by the action of picric ether $C_6H_2(NO_2)_3OEt$ on hydroxylamine (Michael a. Browne, *J. pr.* [2] 35, 358). Silky needles. Its solution is turned brown by the least trace of ammonia.

Hexa-nitro-di-phenyl-hydroxylamine $\{C_6H_2(NO_2)_3\}_2NOH$. *Di-picryl-hydroxylamine.* [170°]. Formed by adding picryl chloride $C_6H_2(NO_2)_3Cl$ in alcoholic solution to an aqueous solution of hydroxylamine (M. a. B.). Yellow crystals, which may be sublimed.

Benzylidene-hydroxylamine $C_6H_5.CH:NOH$ is described as Benzaldoxim, *v.* vol. i. p. 447. According to very recent researches of Beckmann (*B.* 22, 432), when HCl is passed into an ethereal solution of benzaldoxim there is obtained an isomeride. This (β)-benzaldoxim yields the same products on treatment with HCl as the ordinary or (α)-benzaldoxim, and both their ethyl ethers are oily and are split up by HCl into EtCl, NH_4Cl, and benzoic acid. The benzyl ethers of the two oxims, however, are different.

(α)-Benzylidene-benzyl-hydroxylamine $C_6H_5.CH:NOC_7H_7$. Formed, at ordinary temperatures, by the action of benzyl chloride on an alcoholic solution of (α)-benzaldoxim. Oil. Insol. water, sol. alcohol, and ether. Split up by HCl into benzyl chloride, benzoic acid, and NH_4Cl; but under certain conditions it yields benzoic aldehyde and (α)-benzyl-hydroxylamine.

(β)-Benzylidene-benzyl-hydroxylamine

$C_6H_5.CH:NOC_7H_7$ or

$C_6H_5.CH\left<\begin{matrix}O\text{———}\\NC_7H_7\end{matrix}\right>$. [82°].

Formed by the action of benzyl chloride upon (β)-benzaldoxim dissolved in alcohol containing NaOEt. Formed also from (β)-benzyl-hydroxylamine and benzoic aldehyde. Slender needles (from ether). It forms a crystalline hydrochloride [148°]. On treatment with HCl it yields benzoic aldehyde and (β)-benzyl-hydroxylamine.

Other derivatives of hydroxylamine are described as oxims of aldehydes, ketones, and ketonic compounds generally, and as nitroso-, isonitroso-, or oximido- compounds.

HEXA-HYDRO-XYLENE *v.* Xylene hexahydride.

HYDRO-*o*-XYLOQUINONE $C_6H_2Me_2(OH)_2[1:2:3:6]$. [221°]. Formed by reducing *o*-xyloquinone with SO_2 (Nölting a. Forel, *B.* 18, 2673). Separates from water in crusts. Partially decomposed on melting.

Hydro-*m*-xyloquinone $C_6H_2Me_2(OH)_2[1:3:2:5]$. [151°]. Obtained by reducing *m*-xyloquinone (Nölting a. Th. Baumann, *B.* 18, 1151).

Hydro-*p*-xyloquinone $C_6H_2Me_2(OH)_2[1:4:2:5]$. *Hydrophlorone.* [212°] (N.); [208°] (Carstanjen, *J. pr.* [2] 23, 421). Obtained by passing SO_2 into a saturated aqueous solution of p-xyloquinone (phlorone) (Von Rad, *A.* 151, 164; Nietzki, *B.* 13, 472). Colourless pearly plates (from water). May be sublimed. Sl. sol. cold, m. sol. hot water; v. sol. alcohol and ether; m. sol. boiling benzene. $FeCl_3$ and other oxidising agents readily re-convert it into *p*-xyloquinone. Ammonia turns its solutions brown. It reduces boiling cupric acetate solution with ppn. of Cu_2O. It reduces silver nitrate.

Di-ethyl ether $C_6H_4Me_2(OEt)_2$: [106°]; glittering plates (from alcohol) (Staedel a. Hölz, *B.* 18, 2919).

HYDRUVIC ACID *v.* Pyruvic acid.

HYDURILIC ACID $C_8H_6N_4O_6$ *i.e.*

$CO\left<\begin{matrix}NH.CO\\NH.CO\end{matrix}\right>CH:CH\left<\begin{matrix}CO.NH\\CO.NH\end{matrix}\right>CO$?

Formation.—1. Discovered by Schlieper (*A.* 56, 11) among the products of the action of dilute nitric acid on uric acid, being found on one occasion in the mother-liquor from which alloxan had crystallised. He was, however, unable to repeat the experiment.—2. By heating dialuric acid with glycerin (which acts merely as a solvent) at 160°, the products being acid ammonium, hydurilate, formic acid, and CO_2, thus: $5C_4H_4N_2O_4 = 2C_8H_5(NH_4)N_4O_6 + H_2CO_2 + 3CO_2$ (Baeyer, *A.* 127, 11).—3. By heating air-dried alloxan at 170°, the products being hydurilic acid, formic acid, CO_2, ammonia, and CO (Murdoch a. Doebner, *B.* 9, 1102). The same products are obtained by heating air-dried alloxantin for three or four hours in a sealed tube at 170°. 4. Among the products obtained by passing H_2S for several hours through a boiling solution of alloxantin.—5. By heating uric acid with H_2SO_4 at 130°, glycocoll being also formed, while CO_2 is given off (Schultzen a. Filehne, *B.* 1, 150).— 6. By treating di-bromo-barbituric acid with a small quantity of HI (Baeyer, *A.* 130, 133).

Preparation.—9 pts. of perfectly dry dialuric acid are mixed in a capacious flask with 5 pts. of glycerin, and heated in an oil-bath to 140°–150°. A brisk and regular evolution of carbonic anhydride then takes place, and as soon as this ceases, and the contents of the flask have become solid, the temperature is raised for a short time to 160°, and the glycerin, after cooling, is removed by washing. A yellowish-white granular powder is then left, consisting of acid hydurilate of ammonium. To obtain the free acid the crude ammonium-salt is dissolved in boiling water, ammonia is added in slight excess, and solution of cupric sulphate is added to the filtrate. The liquid then assumes a dark-green colour, and, if hot, deposits on cooling red warty crystals of neutral hydurilate of copper. This salt is then decomposed by hot hydrochloric acid, and the hydurilic acid which crystallises out is washed with dilute hydrochloric acid and dried over the water-bath.

Properties.—Crystallises from water in small four-sided prisms (containing 2aq). From a hot concentrated solution in HClAq, or from an ammoniacal solution by ppn. by HCl, it separates as a crystalline powder composed of small tablets (containing aq). V. sl. sol. cold, m. sol. hot, water; v. sl. sol. alcohol. Dissolves in conc. H_2SO_4, and is reppd. unaltered on adding water. Scarcely sol. aqueous HCl. Not attacked by reducing agents. Not attacked by aqueous alkalis; melting potash slowly forms oxalic acid. Gives a dark-green colour with $FeCl_3$. This colour is also given by its soluble salts, but is destroyed by strong acids and alkalis; heat also destroys it, changing it to red.

Reactions.—1. When heated with *ferric chloride* it yields oxy-hydurilic acid, characterised by producing a blood-red colour with ferric salts.—2. HCl mixed with $KClO_3$ forms di-chloro-hydurilic acid.—3. Fuming *nitric acid* gives only alloxan; nitric acid of S.G. 1·4 gives alloxan, violuric acid (nitroso-barbituric acid), violantin, and dilituric acid, the last named being the ultimate product when heat is employed.

Salts.—Hydurilic acid is dibasic. It is a strong acid, and can decompose metallic chlorides, expelling HCl and forming acid salts. It dissolves readily in aqueous alkalis, and the solutions give pps. with metallic salts; the pps. are, however, acid salts. The neutral salts must be prepared from the free acid. HCl added to solutions of salts of hydurilic acid ppts. the acid as a chalk-white amorphous powder, which, when placed in hot water or hot HClAq, becomes crystalline.—NH_4HA'': small octahedra (by ppn. of an ammoniacal solution by acetic acid). M. sol. boiling water, separating as granules and crusts on cooling.—$(NH_4)_2A''$aq: needles, separating on rapidly cooling a hot saturated solution. Obtained in the same form by ppn. with ammonium sulphide, in which it is insoluble.—$(NH_4)_2A''$2aq: large shining monoclinic efflorescent prisms, obtained by slow evaporation; m. sol. water, v. sol. aqueous NH_3, but reppd. by alcohol.—Na_2A'' 4aq: small prisms; obtained by dissolving the acid in NaOHAq, acidulating with acetic acid, and ppg. with alcohol.—BaA'' aq: amorphous pp., soon becoming crystalline, got by adding a hot solution of hydurilic acid to barium acetate.—$CaH_2A''_2$ 8aq: small shining prisms, which separate when hydurilic acid is added to a solution of $CaCl_2$.—CaA'' 3aq: amorphous pp., soon becoming crystalline, obtained by decomposing calcium acetate by hydurilic acid.—$CuH_2A''_2$ 8aq. Obtained by mixing the acid with cupric acetate or with cupric sulphate. Separates from concentrated solutions in green needles, from more dilute solutions in yellow prisms. When heated the anhydrous salt is left as a red powder, which may also be obtained by ppn. from hot solutions.—CuA'' 4aq. Obtained by adding the acid to excess of cupric acetate, or by mixing the neutral ammonium salt with cupric sulphate. From cold solutions it is ppd. in short red needles of the hydrated salt; from warm concentrated solutions as a brownish-red pp. of the anhydrous salt.—$ZnH_2A''_2$: feathery groups of lustrous needles, which separate when a solution of $ZnCl_2$ is mixed with hydurilic acid.—ZnA'' 2aq: white amorphous pp., soon becoming crystalline.

Di-chloro-hydurilic acid $C_8H_4Cl_2N_4O_6$. Prepared by adding $KClO_3$ in small portions to a pasty mixture of hydurilic in conc. HClAq. Snow-white powder; v. sl. sol. water. Purified by dissolving in H_2SO_4 and reppg. by water, when it separates as small trimetric crystals (containing 2aq). Warm nitric acid slowly converts it into dilituric acid.—K_2A'' 2aq: small six-sided tables (from water): sl. sol. cold water.

HYGRINE. A volatile alkaloid said to accompany cocaïne in coca leaves (Wöhler a. Lossen, *A.* 121, 374). The leaves are exhausted with distilled water at 70°, the extract ppd. with lead acetate, freed from lead by ppn. with aqueous Na_2SO_4, rendered slightly alkaline by Na_2CO_3, and extracted with ether. The ether extracts cocaïne, and if the residual solution be now rendered strongly alkaline by Na_2CO_3, ether will extract hygrine together with a neutral oil. These may be partially separated by distillation in a current of hydrogen, the greater part passing over below 140° (Lossen). Thick yellow oil, with strong alkaline reaction, burning taste, and characteristic smell resembling tri-methylamine. Fumes with HCl. Slightly volatile with steam. M. sol. water, sol. alcohol and ether. Its aqueous solution gives a white pp. with $SnCl_4$, and a light blue pp. with $CuSO_4$, not reduced on boiling. It also ppts. $HgCl_2$ and $AgNO_3$. It forms a deliquescent hydrochloride, the aqueous solution of which gives a brown pp. with iodine in KI; a white pp. with $HgCl_2$; yellowish flakes with $PtCl_4$; a yellow powder with picric acid; and a white pp. with tannin. The platinochloride is decomposed by boiling water (O. de Coninck, *Bl.* [2] 45, 131). The above are the properties of the hygrine described by Lossen, who states that it is not poisonous. Stockman (*Ph.* [3] 18, 701) found in *dried* coca leaves a very minute amount of an oily alkaloid with burning taste and strong odour, which, however, was very poisonous. W. C. Howard (*Ph.* [3] 18, 71) obtained, by adding $PtCl_4$ to a solution of crude cocaïne, a semi-crystalline pp. insoluble in water at 80°; this platinochloride contained 18·5 p.c. Pt and yielded a base that gave no crystallisable chloride, did not smell of trimethylamine, and had a bitter taste. Hesse (*Pharm. Zeit.* 1887, 669) came to the conclusion that hygrine was tri-methyl-quinoline, but he worked with only a few grammes of the substance. According to Liebermann (*B.* 22, 675) the so-called hygrine is a mixture of oxygenated bases. He found that crude hygrine, a very dark liquid smelling like piperidine and nicotine, was strongly alkaline, and almost entirely soluble in water. After dissolving in ether, drying with sticks of KOH, and fractionally distilling under 50 mm. pressure, two colourless liquids are obtained, boiling under 50 mm. pressure at 128°–131° and 215° respectively, and having the constitution $C_8H_{15}NO$ and $C_{14}H_{24}N_2O$.

Base $C_8H_{15}NO$. (c. 130° at 50 mm.); (194° cor. at 760 mm.). S.G. $\frac{18}{18}$ ·940. V.D. (H = 1) 68. This base, which is isomeric with tropine, may be distilled in a current of nitrogen.—$B'C_6H_2(NO_2)_3OH$: [148°]; yellow needles, m. sol. cold water.

Base $C_{14}H_{24}N_2O$. (215° at 50 mm.). S.G. $\frac{18}{18}$ ·982. Decomposed by distillation under atmospheric pressure.—Salts.—$B''H_2Cl_2$ (dried at 100°): white crystalline powder.—$B''H_2Au_2Cl_8$: egg-yellow pp. —$B''(C_6H_2(NO_2)_3OH)_2$: crystals (from boiling water); v. sl. sol. cold water.—Methylo-iodide $B''Me_2I_2$: white crystalline powder.

HYMENODICTYONINE $C_{23}H_{40}N_2$. An alkaloid contained in the bark of *Hymenodictyon excelsum* from which it may be obtained by mixing with lime and extracting with chloroform (Naylor, *Ph.* [3] 13, 817; 15, 195). By extremely slow evaporation of its ethereal solution it may be obtained in a crystalline form, but otherwise it is an amorphous deliquescent mass. Its solutions are alkaline in reaction, have a persistent bitter taste, and are optically inactive. Its hydrochloride gives pps. with the usual alkaloidal reagents. Conc. H_2SO_4 gives a lemon-yellow colour changing to wine-red with bronzy lustre.—$B''H_2PtCl_6$: yellow amorphous powder.—$B''H_2Cl_2$.

Ethyloiodide $B''Et_2I_2$: rosettes of needles (from alcohol).

HYOCAFFEÏNE *v.* CAFFEÏNE.

HYOCHOLIC ACID $C_{25}H_{40}O_4$. An acid obtained together with glycocoll, by boiling hyoglycocholic acid with aqueous KOH (Strecker, *A.* 70, 191). Granules (from ether). Scarcely sol. water, v. sol. alcohol and ether. The solution of its ammonium salts is ppd. by solutions of metallic salts.—BaA'_2 (dried at 180°). Sl. sol. water, sol. alcohol.

β-Hyocholic acid $C_{25}H_{40}O_4$. An acid obtained in like manner from (β)-hyoglycocholic acid (Jolin, *H.* 13, 205). It differs from the preceding chiefly in requiring a larger amount of Na_2SO_4 or NaCl to ppt. its sodium salt from aqueous solution.

HYODYSLYSIN $C_{25}H_{38}O_3$. An amorphous substance, homologous with dyslysin, produced by the continued action of boiling hydrochloric acid on hyoglycocholic acid (Strecker, *A.* 70, 189). Insol. water, KOHAq, and aqueous NH_3, sl. sol. boiling alcohol, m. sol. ether.

HYOGLYCOCHOLIC ACID $C_{27}H_{43}NO_5$. Occurs as sodium salt, together with a smaller quantity of hyotaurocholic acid, in pigs' bile (Strecker a. Gundelach, *A.* 62, 205).

Preparation.—Fresh pigs' bile is completely saturated with Na_2SO_4; the mixture is heated for some hours, and then left to cool. The resulting pp. is washed with a conc. solution of Na_2SO_4, dried at 110°, and treated with absolute alcohol. The alcoholic solution of sodium hyoglycocholate is decolourised with animal charcoal, and the salt ppd. by ether. The aqueous solution of the sodium salt is ppd. by H_2SO_4, and the pp. dissolved in alcohol and thrown down again with water. The acid separates in transparent drops.

According to Jolin (*H.* 11, 417) hyoglycocholic acid is accompanied by a smaller quantity of a (β)-isomeride, the sodium salt of which is less readily ppd. by Na_2SO_4. A solution of Na_2SO_4 saturated at 0° ppts. Strecker's acid only.

Properties.—White resin, sl. sol. water, imparting an acid reaction; v. sol. alcohol, insol. ether. It melts under hot water, and then has a silky appearance. Dissolves readily in alkalis and alkaline carbonates. Dextrorotatory, $[\alpha] = 2°$; the sodium salt is optically inactive (Hoppe, *C. C.* 1859, 65). It differs from glycocholic acid by its sparing solubility in water, and by forming pps. insol. water with baryta and lime. A solution of its sodium salt is ppd. by metallic salts, even by NaCl, KCl, and NH_4Cl. It gives Pettenkofer's test for bile.

Reactions.—1. Dilute *sulphuric acid* has no action; conc. H_2SO_4 blackens it with evolution of SO_2.—2. Conc. HNO_3 gives off nitrous fumes, and leaves a yellowish mass, chiefly consisting of oxalic acid and cholesteric acid $C_{12}H_{16}O_7$.—3. Boiling conc. HClAq forms hyodyslysin and glycocoll. Boiling aqueous *potash* acts in like manner.

Salts.—NH_4A'. Ppd. by adding ammonium chloride, carbonate, or sulphide, to fresh pig's bile, or to a solution of the sodium salt. Crystalline powder; v. sol. water, v. sl. sol. conc. solutions of ammonium salts. Decomposed by boiling with water.—$NaA'\frac{1}{2}aq$: white non-deliquescent powder. Its alcoholic solution yields, on evaporation, a transparent varnish. It has a persistent bitter taste.—$KA'\frac{1}{2}aq$: white amorphous mass; ppd. by adding KCl to a solution of the Na salt. Melts under water or alcohol, but when quite dry it does not melt, even at 120°.—$BaA'_2 2aq$: sl. sol. water, v. sol. alcohol,—$CaA'_2 2aq$.—AgA': gelatinous pp. which becomes flocculent on boiling.

(β)-Hyoglycocholic acid $C_{27}H_{43}NO_5$? Remains in the mother-liquor when the ordinary or (α)-hyoglycocholate of sodium is ppd. by ice-cold saturated Na_2SO_4 (Jolin, *H.* 11, 417; 12, 512; 13, 205). When this mother-liquor is evaporated sodium β-hyoglycocholate separates in dark brown oily drops, which solidify to a sticky mass. This is washed with ether, and then presents a white curdy appearance. It is v. sol. alcohol and water. The free acid and its salts greatly resemble their (α)-isomerides, but the salts of the (β)-acid melt, as a rule, more easily, and have a less bitter taste. (β)-hyoglycocholic acid gives Pettenkofer's reaction. The (α)-acid is ppd. by dilute acids more readily than the (β)-acid. The alkaline salts of the (β)-acid are more soluble in water than those of the (α)-acid. The Ba, Ca, and Mg salts of the (β)-acid differ from those of the (α)-acid in dissolving in excess of the sodium salt. The sodium salt of the (β)-acid is dextrorotatory.

HYOSCINE. This name was first used to denote the base, subsequently proved to be tropine, obtained by saponifying hyoscyamine. It was then given to a base that accompanies hyoscyamine (*q. v.*).

HYOSCINIC ACID is identical with TROPIC ACID.

HYOSCYAMINE $C_{17}H_{23}NO_3$. *Duboisine. Daturine.* [109°]. An isomeride of atropine occurring in henbane (*Hyoscyamus niger*) and in other species of *Hyoscyamus* (Geiger a. Hesse, *A.* 7, 270; Höhn a. Reichardt, *A.* 157, 98). It occurs both in the seeds and in the juice of these plants, and is accompanied by hyoscine (Ladenburg, *A.* 206, 282). It accompanies atropine in the seeds of the deadly nightshade (*Atropa Belladonna*); indeed Ladenburg (*B.* 21, 3065) is of opinion that atropine is an optically inactive base standing to hyoscyamine in the relation of racemic acid to lævotartaric acid. From 20 g. of commercially pure atropine aurochloride Ladenburg isolated by recrystallisation 1 g. of hyoscyamine aurochloride, and to this he attributes the statement that atropine can be converted into hyoscyamine. Hyoscyamine occurs, mixed with atropine, in the seeds of *Datura Stramonium* (Pesci, *G.* 12, 39; Ladenburg, *C. R.* 90, 874; E. Schmidt, *A.* 208, 196), and in the leaves and twigs of *Duboisia myoporoides* (F. v. Müller a. Rummel, *C. J.* 35, 32; Gerrard, *Ph.* [3] 8, 787; Ladenburg a. Petersen, *B.* 20, 1661). Hyoscyamine mixed with hyoscine occurs in the root of *Scopolia japonica*; hyoscyamine also occurs in the root of *Scopolia Hladnackiana* (E. Schmidt a. Henschke, *Ar. Ph.* [3] 26, 185, 214).

Preparation.—Henbane seeds are extracted with boiling alcohol (90 p.c.) acidulated with tartaric acid, and when the alcohol is distilled off the residue separates into two layers. The upper layer is a green oil, which is shaken with dilute H_2SO_4, and the acid liquid, after nearly neutralising with K_2CO_3, is filtered and evaporated to a syrup. When alcohol is added to this syrup K_2SO_4 separates, and the alcoholic solution must be freed from alcohol by distillation, mixed with a little water, and shaken with K_2CO_3 and chloroform. The alkaloid is extracted from the chloroform by dilute H_2SO_4, and the acid solution, decolourised by animal charcoal, evaporated, and allowed to stand in contact with $CaCO_3$. The liquid is finally mixed with sand, evaporated over H_2SO_4, and the alkaloid extracted by chloroform, from which it crystallises in long prisms (Duquesnel, *J. Ph.* [5] 5, 131).

Properties.—Needles (from dilute alcohol), or prisms (from $CHCl_3$). More soluble in water and dilute alcohol than atropine. Lævorotatory: $[\alpha]_D = -21°$. It enlarges the pupil of the eye in the same way as atropine. It will not sublime (Blyth).

Reactions.—1. Converted into atropine by heating for 5 or 6 hours above its melting-point (E. Schmidt, *B.* 21, 1829). The optical activity of hyoscyamine may likewise be diminished by allowing its alcoholic solution to stand in the cold after a slight addition of one of the following bases: NaOH, KOH, NH_3, NMe_2H, and NMe_4OH (Will, *B.* 21, 1717; Will a. Bredig, *B.* 21, 2777). The optical activity cannot be reduced below $[\alpha]_D = -1·89°$ by this method, so that if Ladenburg is correct in holding atropine to be optically inactive, the conversion of hyoscyamine into atropine is incomplete.—2. Split up by boiling dilute HCl into the same products as atropine, viz.: tropine and tropic acid (Ladenburg, *B.* 13, 607). Baryta-water gives the same products.

Salts.—$B'HAuCl_4$: [159°] (L.); [162°] (Will); golden leaflets with brilliant lustre (Ladenburg, *B.* 13, 10[illegible]). The corresponding aurochloride of atropine melts at 137° and has no lustre. The atropine aurochloride melts under water, that of hyoscyamine does not. Hyoscyamine aurochloride is less soluble in water at 60° than atropine aurochloride.—$B'_2H_2SO_4$ (dried at 100°). Slender needles. [206°].—**Cadmioiodide**: needles (from alcohol); almost insol. water.—**Hydrobromide**: compact prisms (from water).—**Picrate**: yellow oily pp. quickly changing to rectangular plates. —**Platinochloride**: triclinic (Fock, *B.* 21, 1720).

Hyoscine $C_{17}H_{23}NO_3$. *Amorphous hyoscyamine.* Colourless syrupy fluid. Occurs in the mother-liquor from which hyoscyamine has crystallised. It closely resembles hyoscyamine, both in its mydriatic action on the pupil of the eye and in other respects. Boiled with water it splits up into tropic acid and pseudotropine. Solution of hyoscine hydrochloride is precipitated by $HgCl_2$, HgK_2I_4, and K_4FeCy_6.

Salts.—$B'HAuCl_4$: [198°]; yellow prisms. —$B'HI\frac{1}{2}aq$: (dried at 100°); small monoclinic prisms; $a:b:c = ·938:1:1·357$. M. sol. water.—$B'HBr3\frac{1}{2}aq$: trimetric prisms; $a:b:c = ·601:1:·411$; v. e. sol. water.—$B'_2H_2PtCl_6$: octahedral crystals, sol. water and ether-alcohol.—**Picrate** $B'C_6H_2(NO_2)_3OH$: prisms (Ladenburg, *B.* 13, 1549; 14, 1870).

HYOTAUROCHOLIC ACID $C_{27}H_{45}NSO_6$ (?). Occurs in very small quantity in pigs' bile (Strecker, *A.* 70, 180). Apparently split up by boiling with HCl into taurine and hyocholic acid.

HYPO-. *Use of this prefix applied to inorganic compounds*: for *hypo- compounds v.* the element the hypo- compound of which is sought for, or the salts to the name of which hypo- is prefixed. Thus *hypo-bismuthic oxide* will be found under BISMUTH, OXIDES OF; *hypo-bromous acid* and *hypo-bromites* will be found under BROMINE, OXY-ACIDS OF; *hypo-phosphites* will be found under PHOSPHORUS, OXY-ACIDS OF.

HYPOGÆIC ACID. This name was given by Gossmann a. Scheven (*A.* 94, 230) to an acid of the oleïc series $C_{16}H_{30}O_2$, melting at 33°, supposed to exist in earth-nut oil (*cf.* Schröder, *A.* 143, 22; Caldwell a. Gössmann, *A.* 99, 310). According to Schön (*A.* 244, 253), however, no such acid can be obtained from the oil, which contains oleïn and not its lower homologue.

HYPOQUEBRACHINE $C_{12}H_{26}N_2O_2$. [80°]. An alkaloid occurring in quebracho bark (Hesse, *A.* 211, 264). It is a strong base with bitter taste, v. sol. alcohol, ether, and chloroform. Forms yellow amorphous salts.—$B'_2H_2PtCl_6$ 4aq.

HYPOXANTHINE $C_5H_4N_4O$. *Sarcine. Sarkine.* S. ·33 in the cold; 1·28 at 100°. S. (alcohol) ·11 at 78°. Occurs in the spleen of men and oxen (Scherer, *A.* 73, 328), in the bone-marrow of men and calves (Heymann, *Pf.* 6, 194). Occurs also in the muscular tissue of horses, oxen, and hares (Strecker, *A.* 108, 137), and in the blood of corpses (Salomon, *H.* 2, 94). It is a product of the reduction of uric acid $C_5H_4N_4O_3$ by sodium-amalgam (Strecker a. Rheineck, *A.* 131, 121). It is formed from blood-fibrin by the action of pancreas-ferment, and in much smaller quantity by the simple decay of blood-fibrin (Krause a. Salomon, *B.* 11, 574; 12, 95; 13, 1160); in both cases its formation may be due to the presence of nucleïn in the blood-fibrin, since it is not formed from purified fibrin (Kossel, *H.* 5, 156; Chittenden, *J. Th.* 1879, 61). Formed, together with xanthine, leucine, tyrosine, guanine, and carnine, in the decomposition of the proteïd constituents of yeast (Schützenberger, *Bl.* [2] 21, 204; Kossel, *H.* 3, 291). Hypoxanthine is also formed by the action of chlorine-water on carnine $C_7H_8N_4O_3$ (Weidel, *A.* 158, 362). Hypoxanthine accompanies caffeïne and xanthine in tea (Baginsky, *H.* 8, 395).

Preparation.—Extract of meat is dissolved in water and ppd. with lead subacetate. The filtrate is freed from lead by H_2S, concentrated, and ppd. with ammonia and $AgNO_3$. The pp. is dissolved in the smallest possible quantity of dilute HCl (S.G. 1·1). The compound of hypo xanthine and $AgNO_3$ separates on cooling, and is subsequently decomposed by H_2S (Neubauer, *Fr.* 6, 41).

Properties.—Minute crystals, sl. sol. water, v. sl. sol. alcohol. Readily soluble in acids and alkalis. Ppd. by CO_2 from its solution in aqueous KOH. Neutral to litmus. Ppd. by phosphomolybdic acid in acid solution. According to Kossel (*H.* 6, 428) it cannot be oxidised to xanthine as formerly supposed.

Salts.—$C_5H_4N_4OHCl$ aq: tables.—$(C_5H_4N_4O)_2H_2PtCl_6$: yellow crystals, sl. sol. cold, very soluble in hot, water.—$C_5H_4N_4OHBr$.—$C_5H_4N_4OHNO_3$; (at 100°): large crystals.—$C_5H_4N_4OBaO_2H_2$: crystals.—$C_5H_2Ag_2N_4O$ ½aq: gelatinous pp.—$C_5H_4N_4OAgNO_3$: flocculent pp. Crystallises from boiling HNO_3 in small scales. Dissolves in 4,960 pts. of cold dilute HNO_3 (S.G. 1·1). The ppn. of hypoxanthine by $AgNO_3$ is prevented by the presence of gelatin in the solution (Salkowski, *Pf.* 6, 91).

HYSTAZARINE *v.* DI-OXY-ANTHRAQUINONE.

I

IBOTIN. A glucoside said to occur in the aqueous extract of the seeds of *Ligustrum Ibotu* (Martin, *Ar. Ph.* [3] 13, 338). The solution is ppd. with lead acetate, and the pp. decomposed by H_2S and exhausted with alcohol. It is a yellowish-white powder. Conc. H_2SO_4 dissolves it, forming a red solution, which loses its colour on addition of water.

ICACIN $C_{45}H_{74}O$ or $(C_5H_8)_9H_2O$ (Flückiger); $C_{46}H_{76}O$ (Stenhouse a. Groves, *A.* 180, 255; *C. J.* 29, 175); $C_{47}H_{77}(OH)$ (Hesse, *A.* 192, 181). The last formula represents it as amyrin in which one hydroxyl has been displaced by hydrogen. Icacin is the crystalline resin of conima or Incense resin (Scribe, *A. Ch.* [3] 13, 166). Steam-distillation expels an essential oil, conimene (*q. v.*), the remaining resin being almost entirely soluble in alcohol, from which it is deposited in silky needles on cooling. It may be purified by recrystallisation from ligroïn. It crystallises in needles [175°]. Insol. water, m. sol. boiling alcohol and petroleum, v. sol. ether, CS_2, and hot benzene. Hot conc. H_2SO_4 blackens it.

***n*-ICOSANE** $C_{20}H_{42}$. [36°]. (205° at 15 mm.). S.G. $\frac{37}{4}$ ·778; $\frac{80}{4}$ ·749; $\frac{100}{4}$ ·736. Formed by reduction of the dichloride of heptyl tridecyl ketone with HI and P. Produced by treating *n*-decyl iodide with slices of sodium; the reaction which begins in the cold is finished by heating to 150°, and the product is mixed with alcohol, water being then added, and the hydrocarbon rectified and finally crystallised from ether-alcohol. Obtained also by fractionating paraffin from brown coal (Kraff, *B.* 15, 1717; 19, 2220; 21, 2262).

ICOSINENE $C_{20}H_{38}$. *Eicosylene.* (315°). S.G. $\frac{24}{}$ ·818. Prepared from ozokerit, or the solid paraffin [37°] from brown coal by heating with PCl_5 at 170° and distilling the resulting $C_{20}H_{40}Cl_2$ (Lippmann a. Hawliczek, *B.* 12, 69). Combines with Br and Cl forming oily $C_{20}H_{38}Br_2$ and $C_{20}H_{38}Cl_2$ (*v.* DI-CHLORO- and DI-BROMO-ICOSYLENE).

ICOSONENE $C_{20}H_{36}$. *Didecene.* (330°–335°). S.G. $\frac{12}{}$ ·936. $[\alpha]_D = -2°$. Obtained from the fraction (330°–340°) of the product of the distillation of colophony, by removing other unsaturated hydrocarbons by treatment with H_2SO_4 or HNO_3 (Renard, *C. R.* 106, 1086). Colourless, non-fluorescent, oil. Does not alter when exposed to air, and is not affected by H_2SO_4, by HNO_3, by HCl, or by bromine in the cold. Occurs to the extent of 10 p.c. in the resin oil.

IDRIALIN $C_{80}H_{54}O_2$. The essential constituent of idrialite, a mineral found mixed with cinnabar in the mercury mine of Idria (Dumas, *A.* 5, 16; Schrotter, *A.* 24, 336; Laurent, *A. Ch.* [2] 66, 143; Bödeker, *A.* 52, 100; Goldschmiedt, *J.* 1879, 365; *B.* 11, 1579). Extracted by boiling idrialite with xylene. Glittering plates. May be distilled in a current of CO_2. Almost insol. alcohol and ether, v. sol. boiling oil of turpentine, v. e. sol. CS_2. Fuming H_2SO_4 forms a sulphonic acid. It gives no acetyl derivative. Oxidised by chromic acid to palmitic and stearic acids and oxyidrialin $C_{80}H_{46}O_{10}$, a red substance which forms a deep-violet solution in H_2SO_4. Oxyidrialin may be reduced to idrialin by distillation with zinc-dust, but it gives stearic acid when distilled in a current of hydrogen.

Bromine-water converts idrialin into $C_{80}H_{36}Br_{18}O_2$. Br in HOAc forms $C_{80}H_{42}Br_{12}O_2$, a reddish-yellow powder, v. sol. hot chloroform and benzene. Boiling conc. HNO_3 forms $C_{80}H_{43}(NO_2)_{11}O_2$. Fuming HNO_3 produces $C_{80}H_{34}(NO_2)_{16}O_2$.

IDRYL is identical with FLUORANTHENE (*q.v.*).

IGASURINE is impure BRUCINE (Shenstone, *C. J.* 39, 457).

ILICYL ALCOHOL $C_{25}H_{44}O$ (Personne, *C. R.* 98, 1585; *Bl.* [2] 42, 150); $C_{22}H_{38}O$ (Divers a. Kawakita, *C. J.* 53, 274). [175°] (P.); [172°] (D. a. K.). (above 350°). Birdlime, obtained by fermentation of the inner bark of the holly *Ilex Aquifolium*, is a greenish tenacious substance, which when dried at 100° and extracted by chloroform or ligroïn leaves an ash mainly composed of calcium phosphate. The evaporated extract contains a compound ether, which may be saponified by alcoholic KOH. An elastic substance resembling caoutchouc separates, and when the liquid portion is poured into water a gelatinous pp. is obtained, which can be purified by repeated crystallisation from alcohol. Needles (from alcohol or by sublimation); insol. cold water, m. sol. alcohol, miscible with boiling light petroleum, ether, and chloroform. On heating with palmitic acid a substance resembling birdlime is formed.

Acetyl derivative [206°].

ILIXANTHIN $C_{17}H_{22}O_{11}$. [198°]. Occurs in the leaves of the holly (*Ilex Aquifolium*). Obtained from the leaves gathered in August by extracting them with dilute (80 p.c.) alcohol, removing the greater part of the alcohol by distillation, washing with ether the granules which separate in a few days, and recrystallising from alcohol and hot water (Moldenhauer, *A.* 102, 346). Minute straw-yellow needles. Decomposes with ebullition at 215°. Nearly insol. cold water, v. sol. hot water, forming a yellow solution; sol. alcohol, insol. ether. It does not reduce boiling Fehling's solution. Dissolves in HClAq. Alkalis and alkaline carbonates turn its aqueous solution orange-yellow. $FeCl_3$ colours its solution green. Lead acetate and subacetate give a splendid yellow pp., soluble without colour in acetic acid. Ilixanthin dyes cloth, mordanted with iron or alumina, yellow. A yellow crystalline substance, $C_{15}H_{20}O_{11}$, which may be extracted from the leaves of buckwheat (*Polygonum Fagopyrum*), differs from ilixanthin only in giving an olive-brown colouration with $FeCl_3$ (Schunck, *Chem. Gaz.* 1859, 201).

IMABENZIL *v.* vol. i. p. 467.

IMIDES. Compounds containing the divalent group imidogen NH united to a divalent acid radicle. They are for the most part described under the acids which may be obtained from them by displacing NH by $(OH)_2$.

IMIDO-DI-ACETIC ACID *v.* DI-GLYCOLLAMIC ACID.

DI-IMIDO-*s*-DI-AMIDO-BENZENE $C_6H_2(NH_2)_2(NH)_2$ [1:4:2:5]. The nitrate $C_6H_2(NH)_2(NH_2,HNO_3)_2$ is obtained as a pp. of small green needles by adding an excess of Fe_2Cl_6 to a solution of *s*-tetra-amido-benzene hydrochloride (1 pt.) and ordinary HNO_3 (2 pts.) in water (15 pts.). By solution in conc. H_2SO_4 it is converted into *s*-di-nitro-di-amido-quinone $C_6(NO_2)_2(NH_2)_2O_2$ [1:4:2:5:3:6] (Nietzki, *B.* 20, 2115).

IMIDO-AMIDO-ETHENYL-*o*-AMIDO-PHENYL-MERCAPTAN $C_8H_7N_3S$ probably $C_6H_4{<}\substack{N\\S}{>}C.C(NH_2):NH$. [150°]. Obtained by dissolving *o*-amido-phenyl mercaptan in an excess of alcoholic cyanogen. Colourless needles (from alcohol) or plates (from benzene). Weak base. By heating with aniline it is converted into the mono- and di- phenyl derivatives $C_6H_4{<}\substack{N\\S}{>}C.C(NHPh):NH$ and $C_6H_4{<}\substack{N\\S}{>}C.C(NHPh):NPh$, with evolution of NH_3. Warmed with an alcoholic solution of *o*-amido-phenyl mercaptan it is converted into the anhydro-oxalyl derivative of the latter $C_6H_4{<}\substack{N\\S}{>}C.C{<}\substack{N\\S}{>}C_6H_4$, ammonia being evolved. Cold alcoholic KOH splits off NH_3, giving the acid $C_6H_4{<}\substack{N\\S}{>}C.CO_2H$. Salts.—$B'H_2Cl_2PtCl_4$.—$B'HClAuCl_3$ (Hofmann, *B.* 20, 2252)

DI-IMIDO-AMIDO-ORCIN *v.* AMIDO-DI-IMIDO-ORCIN.

IMIDO-AMIDO-DI-PHENYL SULPHIDE *v.* AMIDO-IMIDO-DI-PHENYL SULPHIDE.

DI-IMIDO-AMIDO-RESORCIN *v.* AMIDO-DI-IMIDO-RESORCIN.

IMIDO-BENZYL ISOAMYL SULPHIDE $C_{12}H_{17}NS$ *i.e.* $C_6H_5.C(NH).S.C_5H_{11}$. Formed by passing HCl into a mixture of isoamyl mercaptan and benzonitrile, and decomposing the resulting crystalline hydrochloride B'HCl with aqueous NaOH (Pinner a. Klein, *B.* 11, 1825). Oil.

IMIDO-BENZYL ETHYL SULPHIDE $C_9H_{11}NS$ *i.e.* $C_6H_5.C(NH).S.Et$. From benzonitrile, mercaptan, and HCl. Also from thiobenzamide and EtI (Bernthsen, *A.* 197, 348). Oil. Readily splits up into benzonitrile and mercaptan. Its alcoholic solution gives pps. with $CuSO_4$ and $HgCl_2$.—B'HCl: [188°]; short thick prisms, v. e. sol. water and alcohol.—$B'_2H_2PtCl_6$: needles.—B'HI: [142°]; monoclinic prisms.

IMIDO-DI-BENZYL SULPHIDE $C_6H_5C(NH).S.CH_2.C_6H_5$. The hydrochloride B'HCl [181°] is formed by heating thiobenzamide with benzyl chloride, or by passing HCl into a mixture of benzonitrile and benzyl mercaptan (Bernthsen, *A.* 197, 350).

IMIDO-BUTYRIC ETHER *v.* ACETO-ACETIC ETHER IMIDE, vol. i. p. 19.

IMIDO-CARBAMINE-THIO-BUTYRIC ACID *v.* THIO-URAMIDO-BUTYRIC ACID.

IMIDO-CARBONIC ETHERS. These compounds, having the formula $NH:C(OR)_2$, are more properly described as ethers of imido-formic orthaldehyde (*q. v.*).

IMIDO-COUMARIN *v.* COUMARIN.

IMIDO-DIETHANE DISULPHONIC ACID *v.* DI-ETHYL-AMINE DI-SULPHONIC ACID.

IMIDO-ETHERS. Compounds containing the group C(OEt)(NH) (Pinner, *B.* 17, 182, 184, 2002, 2007). The hydrochlorides of the imido-ethers are formed by the action of dry HCl on a mixture of a nitrile and an alcohol, dissolved in dry ether. The hydrochloride of a chloro-amido-ether $RCCl(NH_2)(OEt)$ is first formed, but this rapidly splits up into HCl and RC(NH)(OEt). The hydrochlorides of the imido-ethers react with alcohols, forming orthoformic ethers: $RC(NH)(OEt) + 2R'OH = RC(OR')_2(OEt) + NH_3$. Alcoholic NH_3 turns imido-ethers into amidines:

$$RC(NH)(OR') + NH_3 = RC(NH)(NH_2) + HOR'.$$

Primary amines act like ammonia, but potash and tertiary amines do not act upon free imido-ethers.

IMIDO-FORMIC ORTHALDEHYDE $HN:C(OH)_2$. *Imido-carbonic acid.*

Methyl ether $HN:C(OMe)_2$. Obtained like the ethyl ether by reduction of its chloro- derivative $ClN:C(OMe)_2$ (chlorimido-carbonic-methyl-ether) with potassium arsenite. Very volatile.

Ethyl ether $HN:C(OEt)_2$. Prepared by shaking 15 pts. of 'chlorimido-carbonic ether' $(ClN:C(OEt)_2)$ with a solution of 11 pts. of As_2O_3 and 30 pts. of KOH in 120 pts. of water, not allowing the temperature to exceed 50°. Alkaline liquid with odour resembling trimethylamine. Miscible with water but separated by addition of Na or OHKOH. On distillation a large part decomposes. By acids it is decomposed into NH_3 and carbonic ether. By hypochlorites it is converted into 'chlorimido-carbonic ether' (Sandmeyer, *B.* 19, 864). The hydrochloride formed by passing HCl, in the dry ethereal solution, is a thick liquid, which decomposes on heating into urethane and ethyl chloride.

IMIDO-DI-FORMIC ETHER $C_6H_{11}NO_4$ *i.e.* $NH(CO_2Et)_2$. [50°]. (226° at 760 mm.); (145° at 20 mm.). One of the products of the action of chloro-formic acid on potassium cyanate in presence of ether (Wurtz a. Henninger, *C. R*

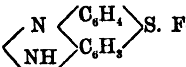
100, 1419; *Bl.* [2] 44, 26). Long prisms. Forms biuret when heated with aqueous NH_3.—$AgC_6H_{10}NO_4$: cubes, blackens at 100°.

β-IMIDO-GLUTAMIC ETHER $CO_2Et.CH_2.C(NH).CH_2.CONH_2$. [86°]. Formed by the action of aqueous ammonia on acetone-di-carboxylic ether $CO(CH_2.CO_2Et)_2$ (Stokes a. v. Pechmann, *Am.* 8, 377). Long, flat, colourless, flexible needles; sl. sol. cold water and ether; sol. hot water and alcohol; m. sol. hot $CHCl_3$. Heated above 86° gives off water and ammonia. Fe_2Cl_6 gives deep red colouration. Soon decomposes in aqueous solution. $PtCl_4$ gives $(NH_4)_2PtCl_6$. $NaNO_2$ in acid solution gives a yellow pp. [178°]. Boiled with Na_2CO_3 it gives di-oxy-amido-pyridine ($C_5H_6N_2O_2$).

IMIDO-HEXOIC ACID. *Nitrile* NH:CEt.CHMe.CN. [48°]. (258°). Formed by the action of Na on propionitrile dissolved in ether, the product being decomposed by water (Meyer, *J. pr.* [2] 38, 336). Plates, sl. sol. water, v. sol. alcohol and ether. Cold conc. HClAq converts it into Et.CO.CHMe.CN. Conc. HClAq at 150° forms di-ethyl ketone, NH_3, and CO_2. Reduced by sodium in alcoholic solution to propylamine.

Imido-di-isohexoic acid. *Nitrile* $HN(C_5H_{10}.CN)_2$. *Imidoisocapro-nitrile.* Formed as a by-product of the action of urea upon valeric-aldehyde-cyanhydrin. The hydrochloride (B'HCl) forms white silky needles, [159°], v. sol. alcohol, insol. ether (Pinner a. Lifschütz, *B.* 20, 2356; *cf.* Erlenmeyer, *B.* 14, 1868).

IMIDO-IMIDO-DIPHENYL SULPHIDE $C_{12}H_8N_2S$ *i.e.*



$\left\langle\begin{matrix}N\\NH\end{matrix}\right\rangle\begin{matrix}C_6H_4\\C_6H_3\end{matrix}\Big>S$

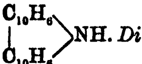
Formed by treating amido-imido-diphenyl sulphide hydrochloride with $FeCl_3$ (Bernthsen, *A.* 230, 103). Brown needles (from dilute alcohol); v. sl. sol. water, m. sol. hot alcohol. Reduced by alcoholic ammonium sulphide to amido-imido-diphenyl sulphide. Its salts dye silk violet.—B'HCl: insol. ether, v. e. sol. water and alcohol.—$B'_2H_2ZnCl_4$: long, dark-violet, needles; m. sol. water.

IMIDO-DI-MALONIC ACID. *Amide* $HN\{CH(CO.NH_2)_2\}_2$. Formed by heating chloromalonic ether with alcoholic NH_3 at 140° (Conrad a. Guthzeit, *B.* 15, 606). Prisms; sol. hot water.

IMIDO-METHYL ALCOHOL *v.* FORMIMIDO-ETHER.

DI-IMIDO-NAPHTHOL *v.* AMIDO-NAPHTHO-QUINONE-IMIDE.

IMIDO-DINAPHTHYL $C_{20}H_{13}N$ *i.e.*



$\begin{matrix}C_{10}H_6\\|\\C_{10}H_6\end{matrix}\Big>NH$

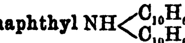
Dinaphthylcarbazole. [216°]. Formed by boiling di-α-amido-dinaphthyl (dinaphthyline) with an excess of HCl or other acid, NH_3 being eliminated (Nietzki a. Goll, *B.* 18, 3259). Crystallises in long colourless needles or silvery plates. Sublimes in colourless needles. It dissolves in H_2SO_4 with a reddish-brown colour, a trace of nitric acid added to this solution produces a dark-green colouration.

Picrate $B'C_6H_2(NO_2)_3OH$: [226°]; red needles (from benzene or alcohol); sublimable.

Acetyl derivative $C_{20}H_{12}NAc$: [above 300°]; colourless plates; sol. acetic acid and alcohol, insol. benzene.

Nitrosamine $C_{20}H_{12}N(NO)$: [above 300°]; small yellow plates; very sparingly sol. ordinary solvents.

Imido-(ββ)-dinaphthyl



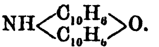
$NH{<}\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}{>}$

[170°]. Obtained by heating (β)-imido-dinaphthyl sulphide with powdered copper in a current of CO_2 (Ris, *B.* 19, 2240). Almost colourless needles; sl. sol. alcohol, v. sol. ether, v. e. sol. benzene. Its solution shows intense bluish-violet fluorescence.

Picrate $B'C_6H_2(NO_2)_3OH$. [221°].

Acetyl derivative $C_{20}H_{12}NAc$. [143°]. Long yellowish needles (from benzene); sl. sol. ether, and alcohol.

IMIDO-DI-NAPHTHYL OXIDE $C_{20}H_{13}NO$ *i.e.*

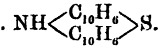


$NH{<}\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}{>}O$

Oxy-di-naphthylamine. [301°]. Formed by heating imido-di-naphthyl sulphide with cupric oxide at 270°, and extracting with boiling benzene (Ris, *B.* 19, 2244). Lemon-yellow crystalline powder (from benzene). Cannot be distilled. Sl. sol. alcohol, ether, HOAc, and boiling benzene; v. sol. H_2SO_4.

Acetyl derivative $C_{20}H_{12}AcNO$. [235°]. Almost insol. alcohol and ligroin, m. sol. ether and benzene.

IMIDO-DI-NAPHTHYL SULPHIDE $C_{20}H_{13}NS$ *i.e.*



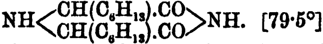
$NH{<}\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}{>}S$

Thiodinaphthylamine. [236°]. Formed by heating di-(β)-naphthylamine (10 pts.) with sulphur (2·4 pts.) for 10 hours, the temperature being slowly raised to 250° (Ris, *B.* 19, 2241). The product is extracted with hot benzene, and boiled with copper powder. Pale yellowish-green needles. Sol. ether and HOAc, v. sol. boiling benzene. Conc. H_2SO_4 forms a violet solution. Distillation over reduced copper forms imido-di-naphthyl. Distillation over CuO at 270° gives imido-di-naphthyl oxide.

Picrate $B'(C_6H_2(NO_2)_3OH)_2$. [c. 256°]. Dark plates or yellow needles; almost insol. alcohol, ether, and benzene.

IMIDO-DI-OCTOIC ACID $C_{16}H_{31}NO_4$ *i.e.* $NH(CH(C_6H_{13}).CO_2H)_2$. *Imido-caprylic acid.* [210°–215°]. Formed, together with formic acid, HCy, and heptoic aldehyde, by boiling its nitrile (1 pt.) with HClAq (15 pts.) for an hour (Erlenmeyer a. Sigel, *A.* 177, 136). When the nitrile is heated with fuming HClAq at 100° it yields the acid and the imide, from which mixture the acid may be extracted by Na_2CO_3Aq. White tasteless powder, which becomes pasty at 180°. Almost insol. cold water and alcohol. Dissolves unaltered in boiling dilute (20 p.c.) HCl, brilliant needles of its hydrochloride separating again on cooling. Strong (40 p.c.) HClAq at 180° resolves it into amido-octoic acid and heptoic aldehyde, $CaH_2A''_2$: cryptocrystalline pp.

Imide $C_{16}H_{30}N_2O_2$ *i.e.*



$NH{<}\begin{matrix}CH(C_6H_{13}).CO\\CH(C_6H_{13}).CO\end{matrix}{>}NH$

[79·5°]. Formed as above. Needles, insol. cold, nearly insol. boiling, water; v. sol. alcohol and ether. B'HCl: minute needles, formed by passing HCl into its ethereal solution. Boiling water splits it up into HCl and the imide. Boiling conc. KOHAq converts it into the acid.

Nitrile $C_{16}H_{29}N_3$. [c. 6°]. From heptoic aldehyde (œnanthol) by combining it with NH_3

and treating the resulting œnanthol-ammonia with HCy. Dilute HCl then dissolves out the nitrile of amido-octoic acid, leaving the nitrile of imido-di-octoic acid undissolved. Thick oil; v. sol. alcohol and ether, v. sl. sol. water and dilute HClAq. Split up by boiling with $AgNO_3$ giving heptoic aldehyde and AgCy. B'HCl: crystals, sol. alcohol; decomposed by water into HCl and the nitrile.

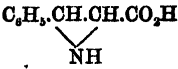
IMIDO-OXY- *v.* Oxy-imido-.

DI-IMIDO-DI-PHENYL-ACETYLENE (?) $C_{14}H_{10}O_2$ *i.e.* $C\lll\begin{matrix}C_6H_4.NH\\C.C_6H_4\end{matrix}>NH$ (?). *Hydrazido-di-phenyl-acetylene. Di-imido-tolane.* [c. 380°]. Formed by treating an alcoholic solution of iso-di-nitro-benzil with tin and HCl (Golubeff, *J.R.* 16, 577). Thin tables. Sublimes at 250°. V. sl. sol. boiling alcohol, forming a solution exhibiting violet fluorescence. HNO_3 (S.G. 1·3) converts it into an amorphous indigo-blue compound. It does not combine with acids.

Benzoyl derivative $C_{14}H_8Bz_2N_2O_2$. [240°]. Pale yellowish needles (from toluene-alcohol), m. sol. boiling benzene, from which it crystallises as $C_{14}H_8Bz_2N_2O_2C_6H_6$ on addition of a little alcohol.

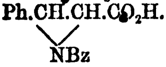
IMIDO-PHENYL-BENZGLYCOCYAMIDINE *v.* vol. i. p. 462.

IMIDO-PHENYL-PROPIONIC ACID

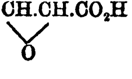


$C_6H_5.\underbrace{CH.CH}_{NH}.CO_2H$. *Imido-cinnamic acid.*

Benzoyl derivative $C_{16}H_{13}NO_3$ *i.e.*



$Ph.\underbrace{CH.CH}_{NBz}.CO_2H$. A body which probably has this constitution is obtained by saponification of its anhydride which is prepared by heating hippuric acid with benzoic aldehyde and acetic anhydride. The acid forms monoclinic needles. [225°]. Sol. alcohol and ether, nearly insol. water. Heated with aqueous HCl or NaOH it yields an acid $C_9H_8O_3$ which is probably the true phenyl-glycidic acid



$C_6H_5.\underbrace{CH.CH}_{O}.CO_2H$ (Plöchl, *B.* 16, 2815).

Benzoyl derivative of the anhydride $C_{32}H_{24}O_5N_2$. [165°]. Yellow needles, sol. hot alcohol, sl. sol. ether, insol. water. Formed as above.

α-IMIDO-DI-PHENYL-DI-PROPIONITRILE $C_{18}H_{17}N_3$ *i.e.* $(Ph.CH_2.CH(CN))_2NH$. Formed together with α-amido-phenyl-propionitrile by the action of NH_3 on the compound of HCN and phenyl-acetic aldehyde (Erlenmeyer a. Lipp, *A.* 219, 191). White crystalline powder [87°] or small needles (from water). Sl. sol. alcohol or ether, insol. petroleum, v. sl. sol. water, m. sol. benzene. From ether it forms six-sided prisms [106°] or rhombic tables [109°], both belonging to the monoclinic system. They are perhaps polymerides.

Salt.—B'HCl: insol. ether.

IMIDO-DI-PHENYL-SULPHIDE $C_{12}H_9NS$ *i.e.* $NH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>S$. *Thiodiphenylamine. Di-phenyl-thiazine.* [180°]. (c. 371° uncor.); (290° at 40 mm.).

Formation.—1. By heating diphenylamine, with sulphur or bodies that give off sulphur, such as S_2Cl_2 (Bernthsen, *A.* 230, 75).—2. By the action of SCl_2 on diphenylamine dissolved in benzene (Holzmann, *B.* 21, 2064).—3. In small quantity by heating *o*-amido-phenyl mercaptan with pyrocatechin for 30 hours at 230° (Bernthsen, *B.* 19, 3255).

Preparation.—By boiling diphenylamine (1,500 g.) with sulphur (580 g.) for 8 hours. The product is distilled in small portions (250 g.) and the distillate (60 g.) fractionated (Bernthsen, *A.* 230, 77; *B.* 16, 2897).

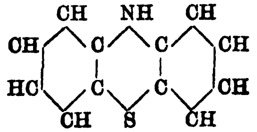
Properties.—Slightly yellowish plates (from alcohol or benzene). Sol. hot alcohol, HOAc, benzene and ether, sl. sol. ligroïn. May be sublimed in plates. Has no basic properties, being insol. dilute HCl. It oxidises readily, the alcoholic solution turning red in air. $FeCl_3$ colours its alcoholic solution dark green. Bromine vapour does the same. The green colour is destroyed by alkalis. HNO_3 colours the solution in HOAc green. Cold conc. H_2SO_4 gives off CO_2 and forms a greenish-brown solution which in thin layers appears rose-red. Hot conc. H_2SO_4 forms a bluish-violet liquid. HNO_3 forms nitro-derivatives which are reduced by $SnCl_2$ to a leuco-base, which on addition of $FeCl_3$ forms a violet dye. Cold alcoholic solutions of imido-diphenyl sulphide give: (*a*) with aqueous $AgNO_3$ a green colour and a black pp.; (*b*) with $PtCl_4$ a green pp.; (*c*) with $CuSO_4$, $HgCl_2$, and $Pb(OAc)_2$, no pps.

Reactions.—1. Distillation over red-hot zinc-dust gives some diphenylamine.—2. By boiling with copper powder it gives CuS and carbazole. 3. By heating with benzoic acid and $ZnCl_2$ there is formed phenyl-acridine.—4. EtBr gives ethyl-imido-di-phenyl sulphide $NEt<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>S$ [102°] which crystallises in long thin white plates.—5. MeI forms the corresponding $SC_{12}H_8NMe$ [100°].

Acetyl derivative $C_{12}H_8AcNS$. [197°]. Prisms. V. sl. sol. hot HOAc, alcohol, and benzene. Its alcoholic solution is not turned green by $FeCl_3$.

Benzoyl derivative $C_{12}H_8BzNS$. [171°]. Plates (from alcohol); m. sol. hot alcohol (Fränkel, *B.* 18, 1844).

Constitution.—The imide group is shown by the ready formation of the acetyl and methyl derivatives. The sulphide character of the sulphur is shown by the oxidation of the methyl derivative to a sulphone. The imido-di-phenyl sulphide itself cannot be oxidised to a sulphone because the imidogen is first attacked. The body does not combine with MeI, but neither does Ph_2S, although Me_2S does. The S is not in *p*- position, because that is still unoccupied. Probably the formula is



which would also be indicated by its formation from *o*-amido-phenyl-mercaptan.

References.—Amido-, Nitro-, Methyl-amido-, and Oxy- imido-diphenyl sulphide.

Imido-di-phenyl disulphide $NH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>S_2$. [60°]. Formed by the action of S_2Cl_2 on diphenylamine dissolved in petroleum ether (Holzmann, *B.* 21, 2063). Small yellow needles, insol. water, v. sl. sol. cold alcohol, ether, and benzene.

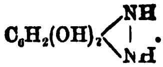
α-IMIDO-DI-PROPIONIC ACID $C_6H_{11}NO_4$ *i.e.* $NH(CHMe.CO_2H)_2$. '*Diethylidenelactamic acid.*' *Didenlactamic acid. Dilactamic acid.* Formed, together with alanine, by treating aldehyde-ammonia with HCl and HCy successively (Heintz, *A.* 160, 35; 165, 44; 202, 375). The product is boiled with lead hydrate, filtered, freed from lead by H_2S, concentrated, and mixed with alcohol. Alanine then separates, and the mother-liquor is mixed with $ZnCO_3$ and evaporated to dryness. The residue of zinc imido-dipropionate is washed with water, and decomposed by H_2S. Minute slender needles, v. sol. water, insol. alcohol.

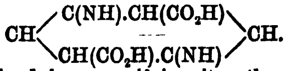
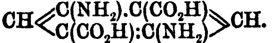
Salts.—NH_4HA'': rectangular tables (from alcohol) or needles (from alcohol-ether). V. sol. water, sl. sol. alcohol, insol. ether.—ZnA'': minute dimetric tables, v. sl. sol. water, v. sol. HClAq.—CdA''aq : minute needles (from water), v. sol. cold water, but can exist also in a less soluble form.—PbA'' : crystalline crusts (ppd. by adding alcohol to the aqueous solution).—CuA'' 3aq: blue grains, v. sl. sol. water and alcohol.—Ag_2A'': white pp.; explodes slightly when heated. May be crystallised from boiling water.—$HA'HCl$: extremely soluble crystals.

Nitrosamine $NO.N(CHMe.CO_2H)_2$. The calcium salt of this acid is formed by treating the acid, dissolved in HNO_3, with calcium nitrite, neutralising with lime, evaporating, and mixing with alcohol and ether. The free acid, obtained from this salt by treatment with oxalic acid, forms flat colourless needles, v. sol. water and alcohol, sol. ether.

Nitrile $C_6H_9N_3$ *i.e.* $NH(CMe.CN)_2$. [68°]. When aldehyde-ammonia (1 mol.) is dissolved in dilute (30 p.c.) HCy (1 mol.), and HCl or H_2SO_4 is added to acid reaction, α-amido-propionitrile separates as an oil. If, after removing this oil, the mixture be allowed to stand for several days, needles of imido-dipropionitrile separate; after some time these are followed by crystals of hydrocyanaldine and finally of para-hydrocyanaldine (Erlenmeyer, *A.* 200, 120; *cf.* Urech, *B.* 6, 1115). It is perhaps one of the products formed by passing a mixture of ammonia and alcohol-vapour over red-hot iron (Monari, *C. R.* 98, 105). Monoclinic needles (from ether); $a:b:c = 1·086:1:1·247$; $\beta = 70° 21'$; m. sol. alcohol and ether, sl. sol. water. Readily sublimes. When heated with dilute HCl it yields α-imido-dipropionic acid. With $AgNO_3$ it gives on warming a pp. of AgCy. Aqueous KOH has no action in the cold, on warming it gives NH_3 and aldehyde. $B'HCl$: white crystalline powder, insol. ether, decomposed by water into HCl and the free nitrile. Nitrosamine $NO.N(CHMe.CN)_2$: pale yellow oil, heavier than water, sol. alcohol and ether.

β-Imido-dipropionic acid $NH(CH_2.CH_2.CO_2H)_2$. Obtained, together with β-amido-propionic acid, by boiling β-iodopropionic acid with NH_3 (Heintz, *A.* 156, 40; *cf.* Mulder, *B.* 9, 1904, who could not obtain it). Syrup, which slowly crystallises. —$PbH_2A''_2$: very slender tables.—Ag_2A'': pp.—$AgHA''AgNO_3$: soluble crystals.

DI-IMIDO-RESORCIN  $C_6H_2(OH)_2\left<\begin{matrix}NH\\|\\NH\end{matrix}\right.$. Formed by oxidation of di-amido-resorcin with Fe_2Cl_6, $K_2Cr_2O_7$ or exposure of the alkaline solution to the air (Typke, *B.* 16, 556). Small spangles. Insol. water. Dissolves in aqueous HCl to a magenta-red solution, in strong H_2SO_4 to a violet solution. By tin and HCl it is reduced again to di-amido-resorcin.

DI-IMIDO-TEREPHTHALIC ACID. *Tetrahydride.*  $CH\left<\begin{matrix}C(NH).CH(CO_2H)\\CH(CO_2H).C(NH)\end{matrix}\right>CH$. This acid is obtained by saponifying its ether with alcoholic KOH and ppg. with HOAc (Böninger, *B.* 21, 1765; *cf.* Baeyer, *B.* 19, 429). It crystallises in greenish-yellow prisms, almost insol. ordinary solvents. It forms a colourless hydrochloride $B'H_2Cl_2$, crystallising in plates. In its colourless derivatives the acid has become the desmotropic di-amido-terephthalic acid  $CH\left<\begin{matrix}C(NH_2).C(CO_2H)\\C(CO_2H):C(NH_2)\end{matrix}\right>CH$.

ω-IMIDO-DI-*m*-TOLUIC ACID [1:3] $C_6H_4(CO_2H).CH_2.NH.CH_2.C_6H_4(CO_2H)$ [1:3]. [above 300°]. Formed by reduction of the acid $C_6H_4(CO_2H).C(NH).S.C(NH).C_6H_4(CO_2H)$ (from *m*-cyano-benzoic acid and H_2S) with zinc and HCl. Crystalline. V. sol. alcohol, ether, benzene, and CS_2; sl. sol. hot water. Sublimable. Its characteristic zinc-salt is v. sol. water, alcohol, ether, benzene, and CS_2 (Brömme *B.* 20, 529).

IMIDO-DI-ISO-VALERONITRILE $C_{10}H_{17}N_3$ *i.e.* $NH(CHPr.CN)_2$. [52°]. Formed, together with α-amido-isovaleronitrile and oxy-isovaleronitrile by treating isobutyric aldehyde-ammonia (25 g.) with (30 g. of) a 30 p.c. solution of HCy in the cold. The product is shaken with dilute (5 p.c.) HClAq (200 g.) and ether. The ethereal solution is dried over calcium chloride, and saturated with HCl, whereupon the hydrochloride of imido-di-isovaleronitrile separates (Lipp, *A.* 205, 1; *B.* 13, 905). The hydrochloride is decomposed by NH_3Aq, and the free nitrile extracted by ether, which leaves it on evaporation as an oil, slowly crystallising over H_2SO_4. Monoclinic prisms ; v. sl. sol. water, v. sol. alcohol and ether.—$B'HCl$. Insol. water, which removes its HCl.

IMINES. Compounds of divalent hydrocarbon radicles with imidogen, *e.g. ethylene-imine* $\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>NH$.

IMPERATORIN $C_{16}H_{16}O_4$ *i.e.* $CH_3.O.C_6H_4.O.C_6H_4.O.CH_2.O.CH_3$? *Peucedanin.* [76°] (Heut). Occurs in the root of masterwort (*Imperatoria Ostruthium*), together with terpenes (170°–220°) (Wackenroder a. Wagner, *J.* 1854, 638) ; and also in the root of *Peucedanum officinale* (Schlatter, *A.* 5, 201 ; Bothe, *J. pr.* 46, 371; Heut, *A.* 176, 71). May be extracted from the root of *Peucedanum* by 90 p.c. alcohol, and recrystallised from ether-ligroïn. Small trimetric six-sided prisms. According to Hlasiwetz a. Weidel (*A.* 174, 69) it melts for the first time at 82°, and afterwards at 75°. Insol. water ; v. sl. sol. cold, v. sol. hot, alcohol ; sol. ether. Has no taste. HNO_3 gives nitro-imperatorin, oxalic acid, and tri-nitro-resorcin. Decomposed by heating with HClAq into MeCl and oroselone $C_{14}H_{12}O_4$. Boiling alcoholic KOH gives formic acid and oroselone.

Nitro-imperatorin, so-called. $C_{12}H_{11}NO_5$? [above 100°]. Plates (from alcohol). Converted by heating in gaseous NH_3 into $C_{12}H_{12}N_2O_4$, which crystallises from alcohol in trimetric prisms, reconverted by acids into 'nitro-imperatorin.'

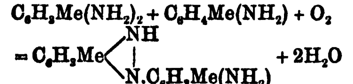
IMPERIALINE $C_{35}H_{61}NO_4$? [254°]. $[\alpha]_D = -35{\cdot}4°$ (in chloroform). Occurs in the bulbs of *Fritillaria imperialis*. Extracted from the bulbs by rubbing up with lime, drying at 100°, and exhausting with hot chloroform. The extract is shaken with water acidified with tartaric acid, the alkaloid ppd. from the concentrated aqueous solution by Na_2CO_3, washed, and recrystallised from alcohol (Fragner, *B.* 21, 3284). The yield is ·1 p.c. Short colourless needles, turning yellow at 240°. V. e. sol. chloroform; m. sol. hot alcohol; sl. sol. ether, benzene, light petroleum, and isoamyl alcohol; v. sl. sol. water. Its solutions have a bitter taste, and are lævorotatory. Solutions of its salts are ppd. by the usual reagents for alkaloids. Conc. H_2SO_4 turns it pale-yellow. A mixture of the base with sugar is turned by H_2SO_4 yellowish-green, pale-green, flesh-colour, cherry-red, and dark violet successively. H_2SO_4 and KNO_3 give an orange-yellow colour. A solution of the base in HClAq is fluorescent, and becomes brownish-green when warmed.—B'HCl: large crystals (from alcoholic HCl); v. sol. water and alcohol.—$B'_2H_2PtCl_6$: yellowish-red crystals (from hot dilute HClAq).—$B'HAuCl_4$: yellow crystals. The aurochloride and platinochloride are both ppd. in oily drops when ether is added to their hot alcoholic solutions, but after washing with ether they may be crystallised from hot dilute HCl. The sulphate is very hygroscopic. The oxalate crystallises only from very concentrated solutions.

INACTOSE. According to Maumené (*Bl.* [2] 32, 652; 48, 773) this inactive sugar may be formed by dissolving silver nitrate (20 g.) in a solution of cane-sugar (20 g.) in water (100 c.c.); after 24 hours the solution becomes dark-brown, and it is then heated to 100°, filtered, and evaporated on a water-bath. The residue is heated to 140°, dissolved in water, and filtered. To free the solution from silver it is treated with a little $CaCl_2$, and filtered; the sugar is then ppd. by alcohol. Inactive syrup. Its solution readily dissolves lime.

INCENSE *v.* CONIMENE, ICACIN, and OLIBANUM.

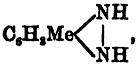
INDAMINES. Colouring matters, the chromogen of which has the general formula $R''\left<\begin{matrix}NH\\NR'\end{matrix}\right>$, where R'' is an aromatic nucleus, the nitrogen atoms occupying the *para-* position to one another, and R' a hydrocarbon radicle (usually aromatic). The colouring matters themselves are derived by the introduction of a basylous or chlorous group into one of the hydrocarbon radicles (usually R'). The indamines may therefore be represented as derived from the (unknown) di-imide of quinone $C_6H_4\left<\begin{matrix}NH\\NH\end{matrix}\right>$, which is probably the true chromogen. In the indamines proper the chromophor is amidogen or alkylated amidogen, the corresponding compounds in which the chromophor is hydroxyl being termed *indophenols*.

Indamines are formed by the oxidation of a mixture of a *p*-diamine with an amine in which the position *para-* to an amidogen is occupied by hydrogen. Thus a mixture of tolylene-*p*-diamine and *o*-toluidine reacts thus:



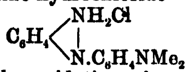
$$C_6H_3Me(NH_2)_2 + C_6H_4Me(NH_2) + O_2 = C_6H_3Me\left<\begin{matrix}NH\\ |\\ N.C_6H_3Me(NH_2)\end{matrix}\right. + 2H_2O$$

(Nietzki, *B.* 10, 1157; Nietzki a. Otto, *B.* 21, 1736). In this reaction we may suppose that the tolylene-*p*-diamine is first oxidised to toluquinone di-imide



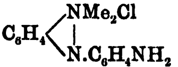
$C_6H_3Me\left<\begin{matrix}NH\\ |\\ NH\end{matrix}\right.$, and that this unstable substance then reacts upon the *o*-toluidine.

The indamine hydrochloride



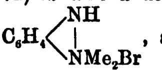
$$C_6H_4\left<\begin{matrix}NH_2Cl\\ |\\ N.C_6H_4NMe_2\end{matrix}\right.$$

obtained by the oxidation of a mixture of *p*-phenylene-diamine with di-methyl-aniline is different from the indamine hydrochloride



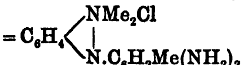
$C_6H_4\left<\begin{matrix}NMe_2Cl\\ |\\ N.C_6H_4NH_2\end{matrix}\right.$ obtained by oxidising a mixture of di-methyl-*p*-phenylene diamine with aniline.

The red dye obtained by oxidising di-methyl-*p*-phenylene-diamine with bromine in HOAc (Wurster, *B.* 12, 2072) is also a derivative of quinone di-imide:

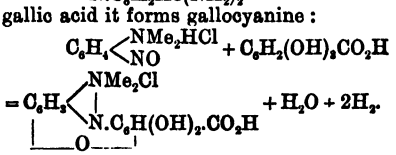


$C_6H_4\left<\begin{matrix}NH\\ |\\ NMe_2Br\end{matrix}\right.$, and reacts with amines forming indamines, and with phenols forming indophenol.

Nitroso-di-methyl-aniline and quinone chlorimide also react with amines and phenols forming indamines and indophenols respectively; thus, nitroso-dimethylaniline hydrochloride acts upon *m*-tolylene diamine, forming tolylene-blue (Witt, *B.* 12, 933): $C_6H_4\left<\begin{matrix}NMe_2HCl\\NO\end{matrix}\right. + C_6H_3Me(NH_2)_2$

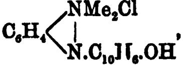


$= C_6H_4\left<\begin{matrix}NMe_2Cl\\ |\\ N.C_6H_2Me(NH_2)_2\end{matrix}\right. + H_2O$, while with gallic acid it forms gallocyanine:

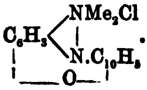


$$C_6H_4\left<\begin{matrix}NMe_2HCl\\NO\end{matrix}\right. + C_6H_2(OH)_3CO_2H = C_6H_3\left<\begin{matrix}NMe_2Cl\\ |\\ N.C_6H(OH)_2.CO_2H\end{matrix}\right. + H_2O + 2H_2.$$

In the last reaction the hydrogen represented as liberated is in reality employed in reducing another portion of the nitroso-di-methyl-aniline (Nietzki a. Otto, *B.* 21, 1740). The (β)-naphthol violet obtained by Meldola (*C. J.* 39, 37) by the action of nitroso-di-methyl-aniline upon (β)-naphthol may also be represented as an indophenol

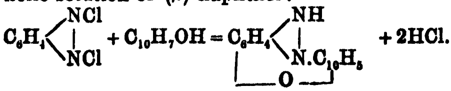


$C_6H_4\left<\begin{matrix}NMe_2Cl\\ |\\ N.C_{10}H_6.OH\end{matrix}\right.$, or perhaps as containing two atoms of hydrogen less:



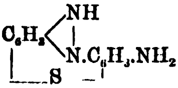
$C_6H_3\left<\begin{matrix}NMe_2Cl\\ |\\ N.C_{10}H_5\end{matrix}\right.$.

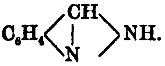
A similar violet dye may be obtained by the action of quinone di-chlorimide upon an alcoholic solution of (β)-naphthol:



$$C_6H_4{<}\begin{smallmatrix}NCl\\ |\\ NCl\end{smallmatrix} + C_{10}H_7OH = C_6H_4{<}\begin{smallmatrix}NH\\ |\\ N.C_{10}H_6\end{smallmatrix}{\underset{O}{\rule{1em}{0.4pt}}} + 2HCl.$$

p-Amido-phenyl-piperidine $NH_2.C_6H_4.N{<}\begin{smallmatrix}CH_2.CH_2\\CH_2.CH_2\end{smallmatrix}{>}CH_2$ reacts like *p*-amido-di-methyl-aniline in the formation of indamines (Lellmann a. Geller, *B.* 21, 2287). Thus, if to a cold neutral solution of *p*-amido-phenyl-piperidine hydrochloride and *m*-phenylene-diamine hydrochloride there be added the calculated quantity of a solution of $K_2Cr_2O_7$, there is formed a deep-blue solution, from which the colouring matter may be ppd. by zinc chloride as a brown powder.

The derivatives of imido-di-phenyl sulphide may be represented as indamines; thus, in Lauth's violet,  $C_6H_3{<}\begin{smallmatrix}NH\\ |\\ N.C_6H_3.NH_2\end{smallmatrix}$ with S, the tinctorial properties need not be connected with the presence of sulphur. The sulphur in Lauth's violet is represented by oxygen in gallocyanine and in (β)-naphthol violet.

INDAZINE $C_7H_6O_2$ *i.e.*  $C_6H_4{<}\begin{smallmatrix}CH\\ |\\ N\end{smallmatrix}{>}NH.$

Indazole. [146·5°]. (270°) at 743 mm. Formed by heating hydrazido-cinnamic acid, when it splits up into acetic acid and indazine

$$C_6H_4(NH.NH_2).CH{:}CH.CO_2H$$
$$= C_6H_4{<}\begin{smallmatrix}CH\\N\end{smallmatrix}{>}NH + CH_3CO_2H$$

(Fischer a. Kuzel, *A.* 221, 280). Formed also by heating sulpho-*o*-hydrazido-cinnamic acid with conc. HClAq at 100° (Fischer a. Tafel, *A.* 227, 309). Slender needles. May be sublimed or distilled. Sl. sol. cold water or alkalis, v. sol. hot water, alcohol, and ether. Sol. dilute HCl. Gives off, when hot, an odour resembling resorcin.

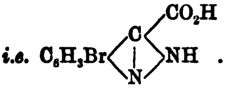
With HCl and $NaNO_2$ in the cold it forms yellow crystals of a nitrosamine, which gives Liebermann's reaction. It does not reduce boiling Fehling's solution. It ppts. several metallic salts. Its hydrochloride separates from alcohol-ether in brownish crystals. Its sulphate forms colourless nodules. The picrate crystallises in yellow needles. Indazine is a much stronger base than indole $C_6H_4{<}\begin{smallmatrix}CH\\NH\end{smallmatrix}{>}CH$, and resists oxidation more powerfully.

Nitrosamine $C_6H_4{<}\begin{smallmatrix}CH\\ |\\ N\end{smallmatrix}{>}N.NO.$ [74°]. Small yellow needles (from benzene).

Bromo-indazine $C_6H_3Br{<}\begin{smallmatrix}CH\\N\end{smallmatrix}{>}NH.$ [124°]. Obtained by heating bromo-indazine carboxylic acid with a large quantity of water at 200°. Colourless needles, sl. sol. cold, m. sol. hot, water.

Di-bromo-indazine $C_7H_4Br_2N_2$. [240°]. Obtained by saturating the warm aqueous solution of bromo-indazine with bromine. Formed also by brominating indazine or indazine hydrochloride in aqueous solution, and by treating bromo-indazine carboxylic acid with bromine-water. Colourless needles, v. sol. alcohol, ether, and hot aqueous NaOH. In alkaline solution it may be reduced to indazine by sodium-amalgam.

Bromo-indazine-carboxylic acid $C_8H_5BrN_2O_2$

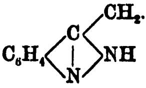


i.e. $C_6H_3Br{<}\begin{smallmatrix}C.CO_2H\\ |\\ N\end{smallmatrix}{>}NH$. Formed by dissolving bromo-indazyl-acetic acid in glacial HOAc, diluting somewhat, and boiling with gradual addition of chromic acid (Fischer a. Tafel, *A.* 227, 303). Small yellowish needles, v. sol. alkalis and alkaline carbonates, almost insol. water and HClAq.

References.—Ethyl-, Methyl-ethyl-, and Ethyl-indazine.

Iso-indazine. This term is given by Fischer and Tafel to $C_6H_4{<}\begin{smallmatrix}CH\\NH\end{smallmatrix}{>}N$, some of the alkyl derivatives of which have been prepared (*v* Ethyl-ψ-indazyl-acetic acid, Di-methyl-ψ-indazine, and Methyl-ethyl-ψ-indazine).

INDAZYL-ACETIC ACID $C_9H_8N_2O_2$ *i.e.*

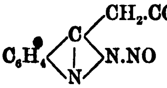


$C_6H_4{<}\begin{smallmatrix}C.CH_2.CO_2H\\ |\\ N\end{smallmatrix}{>}NH$. [170°]. Formed by warming sodium-ν-sulpho-diazo-cinnamic acid (which may be called diazo-cinnamic acid sodium sulphite) $C_6H_4(N{:}N.SO_3Na).CH{:}CH.CO_2H$ with HCl (Fischer a. Tafel, *A.* 227, 303). Prepared by dissolving *o*-hydrazido-cinnamic acid $C_6H_4(NH.NH_2).CH{:}CH.CO_2H$ in alkalis, and shaking with air until it no longer reduces Fehling's solution. The acid is then ppd. by HCl.

Properties.—Slender, yellowish needles, v. e. sol. alcohol, acetic acid, acetone, and hot water, m. sol. ether, v. sl. sol. chloroform, benzene, and ligroin. Dissolves in alkalis and in mineral acids. On distillation it is split up into CO_2 and methyl-indazine. It is completely decomposed by oxidising agents.

Salt.—CuA'_2 2aq: pale green slimy pp., insol. hot water. Crystallises from hot alcohol in slender green needles.

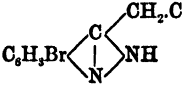
Nitrosamine



$C_6H_4{<}\begin{smallmatrix}C.CH_2.CO_2H\\ |\\ N\end{smallmatrix}{>}N.NO$

Formed by adding a 4 p.c. solution of sodium nitrite to a very dilute solution of indazyl-acetic acid in aqueous H_2SO_4 in the cold. Golden-yellow needles. Insol. water and ligroïn, v. e. sol. ether, chloroform, alcohol, HOAc, alkalis, and warm EtOAc. Reduced by zinc-dust and HOAc to indazyl-acetic acid. It appears to exist in two modifications, one of which decomposes at 90° with evolution of gas, but without melting, while the other, which is obtained by crystallisation from HOAc, melts at 123°.

Bromo-indazyl-acetic acid $C_9H_7BrN_2O_2$ *i.e.*



$C_6H_3Br{<}\begin{smallmatrix}C.CH_2.CO_2H\\ |\\ N\end{smallmatrix}{>}NH$. [200°]. Formed by adding bromine-water to a solution of indazyl-acetic acid in dilute HClAq. Nearly colourless needles (from HOAc), v. sol. alcohol and HOAc, sl. sol. hot water.

INDENE *v.* Indonaphthene.

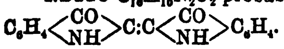
INDIA RUBBER *v.* Caoutchouc.

INDICAN *v.* Indigo.

INDIFULVIN *v.* Indigo.

INDIFUSCIN *v.* Indigo.

INDIGLUCIN *v.* Indigo.

INDIGO $C_{16}H_{10}N_2O_2$ probably  $C_6H_4\left<{CO \atop NH}\right>C{:}C\left<{CO \atop NH}\right>C_6H_4$. *Indigo-blue. Indigotine.* M. w. 262. V.D. 9·45 (for 9·06) (Sommaruga). A blue colouring matter occurring as a colourless glucoside (*Indican*) in various species of *Indigofera, i.e. Indigofera Anil, Indigofera tinctoria*, and in other plants, *i.e. Polygonum tinctorium, Isatis tinctoria*, &c. Commercial indigo, obtained from the juice of the indigofera by fermentation, forms coppery blue lumps, and contains about 50 p.c. of pure indigo, together with indirubin, indifulvin, indirectin, indiglucin, &c.

History.—Indigo was probably one of the earliest known colouring matters, for its employment dates back to the most ancient times. The Egyptian mummy cases were certainly dyed with indigo, and it has been employed in India for many thousands of years (Gerardin, *Journ. de Chim. Med.* 1838, 224). It was well known to the Greeks and Romans, who imported it from India, and hence called it ἰνδικόν or *indicum.* Pliny mentions it, and gives as a test for its genuineness that it should burn with a purple flame when thrown on to glowing charcoal. In the Middle Ages indigo was used for dyeing and painting, but only to a small extent, and so little was known about it that it was generally believed to be a mineral. From the commencement of the sixteenth century the employment of indigo (from *Indigofera*) for dyeing began to rapidly increase. Prior to this time woad (*Isatis tinctoria*) was grown in great quantities in various parts of Europe, especially in Thüringen, and largely employed for blue dyeing (called Persian blue), The importation of indigo from India, which from the sixteenth century rapidly increased, in spite of much protective legislation soon replaced the woad indigo, until at the present time woad is only used as an adjunct to the indigo vat in order to start the fermentation. The present annual production of indigo is estimated as about 8,200 tons (value 4,000,000*l.*) of which 6,100 tons are produced in India, 1,100 tons in America, and 1,000 tons in China and other countries.

Manufacture of commercial indigo.—1. From Indigofera. As carried out in India the process is performed as follows: the cut plants are first steeped in water, where they ferment with evolution of CO_2, the yellow liquor is then run off into another vat, where it is vigorously mixed with air by means of long stirrers. By this means the leucindigo (indigo-white) contained in the solution is oxidised, and the indigo separates out as a blue scum which finally settles to the bottom. The supernatant liquor is then run away, and the indigo is boiled with water for several hours, pressed, and dried. The formation of leucindigo from the glucoside indican, which is present in the plant, is effected by a special bacillus, which is strongly pathogenic and closely resembles the bacilli of pneumonia and rhinoscleroma (E. Alvarez, *C. R.* 105, 286).

2. From woad. The leaves are crushed, the mash is fermented, formed into balls and dried.

Preparation of pure indigo.—1. From commercial indigo: (*a*) Finely powdered indigo (125 g.) and glucose (125 g.) are covered with hot 75 p.c. spirit in a flask of 6 litres capacity. After adding 200 g. of saturated alcoholic NaOH the flask is filled up with hot spirit and left to stand. The clear liquor is then decanted off and left exposed to the air, when the leucindigo (indigo-white) it contains is reoxidised to indigo-blue, which separates in small glistening needles. This is washed with alcohol, water, and finally with HCl, and is then sublimed under 30–40 mm. pressure (Fritzsche, *A.* 44, 290; Sommaruga, *A.* 195, 305).—(*b*) Boiling water (150 pts.) is poured on a mixture of finely-powdered crude indigo (1 pt.) and slacked lime (2 pts.). Ferrous sulphate (1½ pts.) is then added, and the mixture is kept warm for several hours with exclusion of air. The alkaline solution of leucindigo is run into diluted HCl, by which it is precipitated, and by exposure to air is oxidised to indigo.—(*c*) In place of glucose or ferrous sulphate the reduction can be conveniently effected with alcohol and sodium stannite ($SnCl_2$ and excess of NaOH) (Schunck, *Z.* 1865, 671).

2. Synthetically: (*a*) Together with indirubin by reduction of isatin chloride (from isatin and PCl_5) with ammonium sulphide or with HI or zinc-dust and acetic acid. The indirubin is removed by extraction with alcohol (Baeyer, *B.* 11, 1297; 12, 456).—(*b*) Cinnamic acid $C_6H_5.CH{:}CH.CO_2H$ is converted into its ether by means of alcohol and sulphuric acid. This is nitrated at a low temperature with the theoretical quantity of HNO_3 mixed with H_2SO_4. The product is a mixture of about equal quantities of *o* and *p*-nitro-cinnamic ethers $C_6H_4(NO_2)CH{:}CH.CO_2Et$ from which the *ortho-* ether is separated by means of its greater solubility in alcohol. The *ortho-* ether is then converted into the acid by warming with conc. H_2SO_4, dried and converted into the dibromide $C_6H_4(NO_2).CHBr.CHBr.CO_2H$ [1:2] by treatment with an equivalent quantity of bromine. By leaving the dibromide in contact with conc. NaOH the sodium salt of *o*-nitro-phenyl-propiolic acid $C_6H_4(NO_2).C{:}C.CO_2H$ is formed from which the free acid is precipitated by the addition of H_2SO_4, and is filtered off and washed. The *o*-nitro-phenyl-propiolic acid (2 pts.) suspended in cold water (1 pt.) is neutralised with potassium carbonate (1 pt.), and then carefully mixed with potassium xanthate (3 pts.). On allowing the mixture to dry at the ordinary temperature indigo is slowly formed (Baeyer, *B.* 13, 2260; *E. P.* 1880, 1177; *C. C.* 1882, 366). The *o*-nitro-phenyl-propiolic acid can also be converted into indigo by boiling its solution with glucose and sodium carbonate (Baeyer) or with glucose and potassium cyanide (Michael, *J. pr.* [2] 35, 254). (*c*) By adding NaOH (3 pts.) dissolved in cold water (130 pts.) to a solution of *o*-nitro-benzaldehyde (10 pts.) in acetone (15 pts.). The separation of the indigo is complete in two or three days. A better yield is obtained by previously preparing the aldol-like intermediate compound $C_6H_4(NO_2).CH(OH)CH_2.CO.CH_3$ by slowly dropping a 1 p.c. solution of NaOH (about 5 pts.) into a cold solution of *o*-nitro-benzaldehyde (2 pts.) in pure acetone (14 pts.) diluted with an

equal volume of water. The NaOH solution is added until the mixture is slightly alkaline and a trace of indigo begins to be formed; the acetone is then distilled off and the condensation product is left. The latter is converted into indigo by dissolving it without purification in about 250 pts. of boiling water, cooling, and adding NaOH. The yield upon the *o*-nitro-benzaldehyde is 76 p.c. of the theoretical (Baeyer a. Drewsen, *B.* 15, 2856; *Eng. Pat.* 1882, 1266).

Syntheses.—1. By warming isatin $C_6H_4<\begin{matrix}CO\\N\end{matrix}>C(OH)$ with PCl_3, phosphorus, and some acetyl chloride at 70°-80° (Baeyer a. Emmerling, *B.* 3, 515). Isatin (*q.v.*) is formed synthetically by oxidation of amido-oxindole $C_6H_4<\begin{matrix}CH(NH_2)\\NH\end{matrix}>CO$ (Baeyer, *B.* 11, 1228), by reduction of *o*-nitro-phenyl-glyoxylic acid from *o*-nitro-benzoic acid (Claisen a. Shadwell, *B.* 12, 350), or by boiling a solution of *o*-nitro-phenyl-propiolic acid with alkalis (Baeyer, *B.* 13, 2259).

2. Together with indirubin, by adding zinc-dust or HI to an acetic acid solution of isatin chloride $C_6H_4<\begin{matrix}CO\\N\end{matrix}>CCl$, formed from isatin and PCl_5 (Baeyer, *B.* 11, 1297; 12, 457).

3. By the action of ammonium sulphide upon isatin chloride, upon ψ-isatoxim $C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C(NOH)$, or upon isatin ethyl ether $C_6H_4<\begin{matrix}CO\\N\end{matrix}>C(OEt)$ (Baeyer, *B.* 15, 2093; 16, 2203).

4. By the action of air or $FeCl_3$ upon indoxyl $C_6H_4<\begin{matrix}C(OH)\\NH\end{matrix}>CH$, or upon indoxyl-sulphuric acid $C_6H_4<\begin{matrix}C(O.SO_3H)\\NH\end{matrix}>CH$ (Baumann a. Tiemann, *B.* 12, 1098).

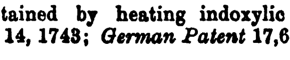
5. In small quantity by oxidation of indole $C_6H_4<\begin{matrix}CH\\NH\end{matrix}>CH$ with ozone (Nencki, *B.* 8, 727).

6. By the action of reducing agents such as glucose, lactose, sulphides or xanthates upon *o*-nitro-phenyl-propiolic acid in alkaline solution, the yield being about 40 p.c. of the 'propiolic acid':

$C_6H_4(NO_2)C{\vdots}C.CO_2H + 2H_2$
$= C_{16}H_{10}N_2O_2 + 2CO_2 + 2H_2O$ (*v. supra*; Baeyer, *B.* 13, 2260).

7. In small quantity by heating *o*-nitro-phenyl-oxyacrylic acid $C_6H_4(NO_2).C(OH):CH.CO_2H$ by itself, or with phenol or acetic acid (Baeyer, *B.* 13, 2263).

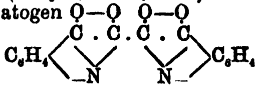
8. Indoxyl $C_6H_4<\begin{matrix}C(OH)\\NH\end{matrix}>CH$, indoxylic acid $C_6H_4<\begin{matrix}C(OH)\\NH\end{matrix}>C.CO_2H$, or ethyl-indoxylic acid $C_6H_4<\begin{matrix}C(OEt)\\NH\end{matrix}>C.CO_2H$ readily give indigo on oxidation with $FeCl_3$, $CuCl_2$, &c. or by atmospheric oxidation of the alkaline solution. Indoxylic acid is obtained from its ethyl ether, which is formed by the action of alkaline reducing agents upon isatogenic ether



. Indoxyl is obtained by heating indoxylic acid (Baeyer, *B.* 14, 1743; *German Patent* 17,656).

9. By warming a mixture of indoxyl or indoxylic acid with *o*-nitro-phenyl-propiolic acid and Na_2CO_3 (Baeyer, *B.* 14, 1743).

10. Diisatogen



formed from the isomeric di-*o*-nitro-di-phenyl-diacetylene $C_6H_4(NO_2).C{\vdots}C.C{\vdots}C.C_6H_4(NO_2)$ by treatment with fuming H_2SO_4, is readily converted into indigo by reduction with ammonium sulphide, zinc-dust and alkalis, glucose and alkalis, &c. With ammonium sulphide in the cold the reduction takes place quantitatively. The di-*o*-nitro-diphenyl-diacetylene is obtained by oxidation with potassium ferricyanide of the cuprous compound of *o*-nitro-phenyl-acetylene $C_6H_4(NO_2).C{\vdots}CH$ which is formed by boiling an aqueous solution of *o*-nitro-phenyl-propiolic acid $C_6H_4(NO_2).C{\vdots}C.CO_2H$ (Baeyer a. Landsberg, *B.* 15, 53; *G. P.* 19,266).

11. By the action of dilute alkalis upon a mixture of *o*-nitro-benzaldehyde $C_6H_4(NO_2)CHO$ with acetone, pyruvic acid, aldehyde, or acetophenone. Acetone and pyruvic acid give the best yields. In these reactions aldol-like condensation products are first formed and are converted into indigo by the further action of the alkali. Thus under the influence of a small quantity of alkali, *o*-nitrobenzaldehyde with acetone gives *o*-nitro-*β*-phenyl-*β*-oxy-ethyl-methyl ketone $C_6H_4(NO_2).CH(OH).CH_2.CO.CH_3$; whilst with aldehyde *o*-nitro-benzoic aldehyde appears to form *o*-nitro-*β*-phenyl-*β*-oxy-propionic aldehyde $C_6H_4(NO_2).CH(OH).CH_2.CHO$, with pyruvic acid *o*-nitro-*β*-phenyl-*β*-oxy-propionyl-formic acid $C_6H_4(NO_2).CH(OH).CH_2.CO.CO_2H$. By treatment with a further quantity of an alkali all these condensation products yield indigo, whilst acetic, formic, or oxalic acid is split off, thus: $2C_6H_4(NO_2).CH(OH).CH_2.CO.CH_3 + 2H_2O = C_{16}H_{10}N_2O_2 + 2CH_3.CO_2H + 2H_2O$ (Baeyer a. Drewsen, *B.* 15, 2856; *E. P.* 1882, 1266).

12. By the action of aqueous alkalis upon *o*-nitro-cinnamoyl-formic acid (*o*-nitro-styryl-glyoxylic acid) $C_6H_4(NO_2).CH:CH.CO.CO_2H$, obtained by saturating a mixture of *o*-nitro-benzaldehyde and pyruvic acid with gaseous hydric chloride at 10°: $2C_6H_4(NO_2).CH:CH.CO.CO_2H = C_{16}H_{10}N_2O_2 + 2CH_3.CO_2H$ (Baeyer a. Drewsen, *B.* 15, 2862).

13. *o*-Nitro-benzylidene-acetone $C_6H_4(NO_2).CH:CH.CO.CH_3$ which is obtained by nitration of benzylidene-acetone, or by heating *o*-nitro-*β*-phenyl-*β*-oxy-ethyl methyl ketone $C_6H_4(NO_2).CH(OH).CH_2.CO.CH_3$ with acetic anhydride, gives indigo by treatment with alcoholic KOH, precipitating with an acid, and then boiling with water or aqueous alkalis. The yield is small (Meister, Lucius, a. Brüning, *E. P.* 1882, 1453; Baeyer a. Drewsen, *B.* 15, 2858).

14. By heating the lactone of *o*-nitro-*β*-phenyl-*β*-oxy-propionic acid with water or acetic acid (Einhorn, *B.* 16, 2212).

15. By bromination or chlorination of acetyl-*o*-amido-acetophenone $C_6H_4(NHAc).CO.CH_3$, or of acetyl-*o*-amido-phenyl-acetylene $C_6H_4(NHAc).C{\vdots}CH$, *eso*-bromo- and chloro-derivatives are obtained. These are converted by conc. H_2SO_4 (10 to 20 pts.) into intermediate products which give indigo on dissolving in aqueous alkalis and exposure to air. Indoxyl

is probably an intermediate product in this reaction (Baeyer a. Bloem, *B.* 17, 963; *German Patent* 21,592).

16. By the action of ammonium sulphide upon the *eso*-mono- or di-chloro- (or bromo-) nitro-acetophenone (*e.g.* $C_6H_4(NO_2).CO.CHCl_2$), formed by chlorination or bromination of *o*-nitro-acetophenone (Gevekoht, *B.* 15, 2084; *A.* 221, 331; *G. P.* 23,785).

17. By heating indoin $C_{32}H_{20}N_4O_5$.

Formation.—In addition to the above synthetical methods indigo is produced: 1. From its glucoside indican by the action of acids and air, by $FeCl_3$, or by fermentation under the influence of a special microbe (Schunck, *J.* 1855, 660; 1857, 564; 1858, 465; *C. N.* 37, 223; 39, 129; Schunck a. Römer, *B.* 12, 2311).—2. The potassium salt of indoxyl sulphuric acid, incorrectly called 'Indican,' is a normal constituent of the urine of animals, being formed in the organism by the oxidation of indole $C_6H_4<\substack{CH\\NH}>CH$, which is a decomposition product of proteids. Indoxyl-sulphuric acid is readily oxidised to indigo by $FeCl_3$, &c., and under certain conditions is converted into indigo in the urine (Schunck a. Hoppe-Seyler, *Arch. Pathol. Anat.* 27, 388; Baumann, *Pf.* 13, 291; Baumann a. Brieger, *H.* 3, 254; Jaffé, *Pf.* 3, 448; Baumann a. Tiemann, *B.* 12, 1098, 1192; 13, 408; Michailow, *B.* 20, 605; *J. R.* 1887, 326; Weber, *B.* 12, 271: Baeyer, *B.* 12, 1600).—3. By oxidation of leucindigo (indigo-white) by air, &c. This reaction performed upon the fibre forms the usual method of dyeing indigo.

Properties.—Pure indigo begins to sublime at 170° (Schunck, *C. J.* 37, 617), forming a purple-red vapour and condensing to dichroic plates belonging to the rhombic system, $a:b:c = \cdot7883:1:\cdot7265$, $\alpha = 76° 30'$, $\beta = 108°$. Under 60-80 mm. pressure it sublimes without any decomposition, and the vapour density has been taken under these conditions by Sommaruga (*A.* 195, 312), and found to correspond to the formula $C_{16}H_{10}N_2O_2$. Insol. water, alcohol, ether; dilute acids or alkalis. V. sl. sol. hot alcohol, amyl alcohol, acetone, or turpentine. Sl. sol. chloroform or acetic acid. V. sol. hot aniline, nitrobenzene, or phenol; from the latter solvents it crystallises on cooling (Stokvis, *J.* 1868, 789; Wartha, *B.* 4, 334; Jacobsen a. Mehu, *J.* 1872, 682). Sol. conc. H_2SO_4 without alteration to a yellowish-green solution, which exhibits a characteristic absorption spectrum between the D and d lines (Vogel, *B.* 11, 1364). The H_2SO_4 solution by long standing or on warming becomes blue from formation of indigo-sulphonic acids.

Reactions.—1. Distilled with KOH it yields aniline (Fritzsche, *A.* 39, 76).

2. It dissolves in boiling aqueous KOH (S.G. 1·45) to a yellow solution of isatic acid and leucindigo (indigo-white): $3C_{16}H_{10}N_2O_2 + 4H_2O = 2C_8H_7NO_3 + 2C_{16}H_{12}N_2O_2$.

3. By fusion with KOH anthranilic acid $C_6H_4(NH_2)CO_2H$ [1:2] is formed (Böttinger, *B.* 10, 269); by heating with KOH at 300° Cahours (*A. Ch.* [3] 13, 113) obtained salicylic acid.

4. By boiling with KOH and MnO_2 it yields anthranilic and formic acids (Böttinger).

5. Oxidising agents, such as chlorine, oxides of chlorine, HNO_3, ferric salts &c., convert it into isatin $C_6H_4<\substack{CO\\NH}>CO$.

6. By damp chlorine it is converted into chlorisatin, dichlorisatin, trichloraniline, and trichlorophenol. Bromine acts in the same way (Erdmann, *J. pr.* 19, 330).

7. With HNO_3 it yields in succession isatin, nitrosalicylic acid, and finally picric acid.

8. Alkaline reducing agents, such as $FeSO_4$ and NaOH, glucose and NaOH, $SnCl_2$ and NaOH, convert it into leucindigo (indigo-white) $C_{16}H_{12}N_2O_2$.

9. By heating with aqueous sodium hydrosulphite Na_2SO_2 and excess of NaOH at 180°, indoline $C_6H_4<\substack{CH:CH.NH\\NH.CH:CH}>C_6H_4$ is formed (Giraud, *B.* 12, 2155). This body is also obtained by heating leucindigo (indigo-white) with zinc-dust and aqueous barium hydrate at 180°.

10. By heating with an excess of saturated HI, hydrocarbons and NH_3 are produced (Berthelot, *Bl.* [2] 9, 189).

11. Unaltered by long boiling with conc. aqueous NH_3 (Liubawin, *J. R.* 15, 17).

12. By digestion of indigo with conc. H_2SO_4 or with slightly fuming H_2SO_4 a mono-sulphonic acid $C_{16}H_9N_2O_2(SO_3H)$ (phœnicine-sulphuric acid) and a di-sulphonic acid $C_{16}H_8N_2O_2(SO_3H)_2$ (sulphindigotic acid) are formed.

13. By reduction to leucindigo (indigo-white) and distillation with zinc-dust it gives a mixture of indole $C_6H_4<\substack{CH\\NH}>CH$ and scatole $C_6H_4<\substack{CMe\\NH}>CH$ (Baeyer, *B.* 13, 2339).

Detection of indigo on fabrics.

(W. Lenz, *Fr.* 26, 535; Prior, *Rep. d. Anal. Chem.* 13, 193, 1884.)

1. A drop of nitric acid gives a bright-yellow spot.

2. When indigo alone is present the following reactions should be given: alcohol extracts no colour even on gentle warming. Cold saturated oxalic acid and borax solutions, 10 p.c. alum solution, and 33 p.c. ammonium molybdate solution, removes no colour even on boiling. Stannous and ferric chloride destroy the colour on warming. Glacial acetic acid dissolves all the colour on repeated boiling, and after mixing the solution with ether and water the aqueous layer is colourless and not coloured by strong hydrochloric acid. When the indigo may be accompanied by other colours the following methods of testing may be adopted.

3. The stuff is warmed with an acidified 10 p.c. solution of $SnCl_2$. Prussian blue remains unchanged. Indigo (vat-blue), indigo-carmine, and aniline-blue (tri-phenyl-rosaniline-tri-sulphonate) are completely removed from the fibre, and yield pale-yellow solutions. Logwood is also removed, but gives a rose-red solution. On adding a large excess of hydrogen peroxide to these solutions the rose-red of logwood is destroyed, aniline-blue gives a blue solution, whilst indigo is not regenerated.

4. Glacial acetic acid dissolves indigo from a fabric. In presence of logwood the cold acid acquires a rose-red colour, which on heating passes into yellowish-red, and is soon obscured by the dissolving indigo. Prussian blue and indigo.

carmine are not dissolved. On mixing the acetic acid solution with ether, and then adding water until the ether separates, the indigo is removed from the aqueous layer, which then in the presence of logwood shows a feeble reddish-yellow tint. If now a few drops of conc. HCl are added, the smallest trace of logwood is revealed by the production of a rich red colour in the aqueous layer. Aniline-blue obscures this reaction.

Estimation.—In fabrics: The dyed stuff (10 g.) is treated in a flask with 200 c.c. of a solution made by adding 2 litres of water and 100 c.c. of milk of lime to 100 c.c. of a solution of Na_2SO_2 prepared from a solution of sodium bisulphite of 35° B. The mixture is heated at 60°-70°, a stream of coal gas being passed through the flask during the reduction. When all the colour has disappeared, a portion of the solution is decanted, cooled, its volume measured, the indigo precipitated by HCl, and after 12 hours' standing collected on a filter, washed, and dried. It is then dissolved with the filter-paper in about 10 c.c. of fuming H_2SO_4, and the solution titrated by the hydrosulphite (Müller's) method (*v. infra*) (Renard, *Bl.* 47, 41).

In commercial indigo: 1. The indigo is reduced to leucindigo (indigo-white) by glucose and NaOH in an aqueous alcoholic solution; the clear solution is separated from the insoluble impurities, and by oxidation with a stream of air the indigo is precipitated and weighed (Rau, *Am. C. J.* 7, 16; Manley, *Chem. Centr.* 1887, 605; Romen's *Journal*, 1887, 16). This gives the value in indigo blue only, as the indirubin remains in the alcoholic solution (Rawson, *S. C. I.* 1885, 491).

2. By reduction with $FeSO_4$ and NaOH and subsequent oxidation (Grace-Calvert).

3. By reduction with sodium hydrosulphite Na_2SO_2 and subsequent oxidation by air. The finely powdered indigo (1 g.) is made into a paste with water and placed in a flask with 500-600 c.c. of lime water; the flask is closed with an indiarubber stopper bored with four holes, one carrying a syphon, another a tap-funnel, the remaining two serve for the entrance and exit of a current of coal gas. The whole is heated at 80°, and 100-150 c.c. of sodium hydrosulphite (equivalent to an ammoniacal copper solution containing 19·04 g. of $CuSO_4$ 5aq per litre) is introduced and kept near the boiling-point for half an hour. After allowing to settle 500 c.c. of the clear liquid are siphoned off, oxidised by aspirating air through it for 20 mins., an excess of HCl added, and the precipitate of indigo and indirubin washed and weighed. The liquid remaining in the flask is measured, and from it is calculated the combined percentages of indigo and indirubin. If the proportion of indirubin is required the filter and precipitate are extracted with alcohol, which dissolves the indirubin. This method gives very good results (Rawson, *C. N.* 57, 7, 19, 29, 34; *S. C. I.* 1885, 489).

4. The indigo is sulphonated and the solution is reduced by a solution of sodium hydrosulphite of known strength, the excess of which is then estimated by titration with ammoniacal $CuSO_4$ (Müller, *J.* 1874, 1019; *Am. Chemist*, 5, 128; Bernthsen a. Drews, *B.* 13, 2283; Rawson, *S. C. I.* 1885, 490).

5. By sulphonation and subsequent oxidation of the sulphonic acid by means of potassium ferricyanide (Allgren), chlorine-water (Bolley), $K_2Cr_2O_7$ and H_2SO_4 (Penny), or $KMnO_4$ (Mohr). The finely powdered indigo (1 g.) is mixed with an equal weight of ground glass, and gradually added to 20 c.c. of H_2SO_4 (S.G. 1·845); it is then placed for 1 hour in a steam-bath at 90°. The sulphuric acid solution is diluted to 1 litre, and 50 c.c. of the filtered solution is mixed with 50 c.c. of water and 32 g. of NaCl. Sodium sulphindigotate being almost insoluble in strong salt solution separates, and after two hours is collected, washed with salt solution (S.G. 1·2), dissolved in hot water, and when cool acidified with 1 c.c. of H_2SO_4, then diluted to 300 c.c., and titrated with $KMnO_4$ (·5 g. per litre). A small correction (+1·6 p.c.) has to be made for the sulphindigotate which remains in the salt solution; the result gives the combined percentages of indigo and indirubin (Rawson, *S. C. I.* 1885, 489).

6. By loss of weight on sublimation (Lee, *Am. C. J.* 6, 185). According to Rawson (*l.c.*) this method is not accurate, since the other compounds present in the crude indigo affect the result; with inferior qualities the result is often too high, whilst in superior qualities it is too low.

7. By spectrum analysis: ·5 g. of the sample is sulphonated and diluted to a litre. This solution is then further diluted according to its depth of colour, and is examined spectroscopically in a layer of 1 c.c. thickness. The coefficient of extinction is directly proportional to the percentage of pure indigo present (Vierordt; Wolff, *Fr.* 17, 310; 23, 29; *D. P. J.* 253, 256).

8. By sulphonation and quantitative dyeing on wool or silk (Chevreul).

Dyeing methods.—Indigo-blue is used for dyeing silk, wool, and cotton, to which it is applied by the following methods:

1. By vat-dyeing, *i.e.* reduction of the indigo to leucindigo (indigo-white) by means of some reducing agent, steeping the material in the colourless solution and finally exposing it to the air, by which the leucindigo is oxidised to indigo, which being insoluble remains firmly fixed in the fibre. This is the best method of indigo dyeing, and gives the fastest colours. Various reducing agents are employed to effect the reduction, and of these different 'vats' the following are the most important:

Cold vats (used chiefly for cotton): *a. Blue vat*, composed of indigo (2 pts.), ferrous sulphate (3 to 4 pts.), slaked lime (3 to 5 pts.), and water (200 pts.). *b. Zinc-dust vat*, composed of indigo (2 pts.), zinc-dust (1 pt.), slaked lime (1 pt.), and water (200 pts.). *c. Hydrosulphite vat*, composed of indigo (1 pt.), 20 p.c. of lime-milk (1 to 1·3 pts.), and the sodium hydrosulphite solution (Na_2SO_2), obtained by reducing 8–10 kilos of sodium bisulphite solution (S.G. 1·275) with zinc-dust or zinc foil, the whole being subsequently diluted with water. *d. Tin salt vat* ($SnCl_2$ and an alkali) is only used for printing. *e. Arsenic vat* (As_2O_3 and an alkali) is only used for printing (*English Patent* 1884, 421; *S. C. I.* 1885, 53). *f. Sugar vat* (glucose and an alkali).

Warm or fermentation vats (only used for wool and silk): *a. Woad vat*, composed of indigo (15 pts.), woad (300 pts.), bran (10 pts.), madder (2 to 15 pts.), slaked lime (12 pts.), and water (4,000 pts.). The liquid is allowed to ferment for about two days, keeping the temperature at 45°–50°, and the vat is then ready for use *b. Potash vat*, composed of indigo (10 pts.), madder (2 to 5 pts.), bran (2 to 5 pts.), and K_2CO_3 (10 to 15 pts.), and water (4,000 pts.), the whole being left to ferment for two days. *c. Soda vat*, composed of indigo (10 pts.), bran (60 to 100 pts.), or treacle (10 to 15 pts.), soda crystals (Na_2CO_3 10aq) (20 pts.), slaked lime (5 pts.), and water (4,000 pts.), fermented for two or three days. For other methods of preparing vats *v.* Goppelsröder, *D. P. J.* 251, 465; 253, 245, 381; *C. S. I.* 1884, 518; Collin a. Benoist, *German Patent* 30,449; *S. C. I.* 1885, 493; Schmückert, *English Patent* 1887, 7,333.

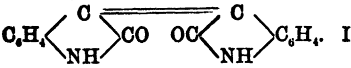
Indigo is also applied to fabrics:

2. By printing with a paste of reduced indigo and developing the indigo by exposure to air.

3. By printing with a paste of sodium *o*-nitro-phenyl-propiolate, sodium or zinc xanthate, borax, and a thickening agent, the colour being slowly developed by leaving the material at the ordinary temperature for two days (Bad. Anil. u. Soda-Fabrik, *E. P.* 1881, 466; *S. C. I.* 1882, 148, 360; 1885, 454). The blue obtained in this way surpasses in purity of shade that obtained with natural indigo, and also has the advantage that it can be readily employed in conjunction with other steam colours, alizarin, &c.; its high price, however, has hitherto prevented its extended application.

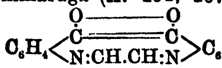
4. By dyeing from a bath of indigo-disulphonic acid ('sulphindigotic acid,' 'indigo-carmine,' or 'indigo-extract'). This method is only employed for wool and silk, as the sulphindigotic acid has no affinity for cotton. The colour obtained by this method, called 'Saxony blue,' although much brighter than 'vat-blue' is not nearly so fast either to soap or light.

Constitution.—The determination of the constitution of indigo is mostly due to A. Baeyer and his pupils. The molecular formula $C_{16}H_{10}N_2O_2$ was established by the vapour density determinations of Sommaruga. Isatin $C_8H_5NO_2$, which is obtained from indigo by oxidation, gives on treatment with reducing agents dioxindole $C_8H_7NO_2$, oxindole C_8H_7NO, and finally indole C_8H_7N (Baeyer a. Knop, *A.* 140, 1, 295). From this Baeyer concluded at that time that indole was the parent substance of the dye-stuff, and represented the latter by the formula $\left.\begin{matrix}C_6H_4C_2HN\\C_6H_4C_2HN\end{matrix}\right\}O_2$. Soon afterwards Strecker proposed for indigo the formula



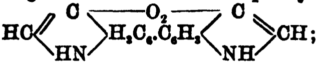
$$C_6H_4\genfrac{}{}{0pt}{}{C}{NH}CO\quad OC\genfrac{}{}{0pt}{}{C}{NH}C_6H_4$$

In 1869 Kekulé (*B.* 2, 748) had assigned to isatin and isatic acid the formulæ $C_6H<\genfrac{}{}{0pt}{}{CO}{NH}>CO$ and $C_6H_4<\genfrac{}{}{0pt}{}{CO.CO_2H}{NH_2}$, thus explaining their ready conversion into *o*-amido-benzoic acid and salicylic acid, and this view was subsequently confirmed by the investigations of Baeyer a. Suida (*B.* 11, 582, 1228) and of Claisen a. Shadwell (*B.* 12, 350). At the same time it was proved that dioxindole and oxindole were respectively the inner anhydrides of *o*-amido-mandelic acid and of *o*-amido-phenyl-acetic acid, and hence were constituted thus: $C_6H_4<\genfrac{}{}{0pt}{}{CH(OH)}{NH}>CO$ (*dioxindole*), $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{NH}>CO$ (*oxindole*). In 1870 Baeyer a. Emmerling (*B.* 3, 517) assigned to indole the formula $C_6H_4<\genfrac{}{}{0pt}{}{CH}{NH}\gg CH$[1:2]. In the same year Emmerling a. Engler (*B.* 3, 885; *cf.* *B.* 9, 1106, 1422) obtained small quantities of indigo by distilling nitro-acetophenone with zinc-dust and soda-lime, from which they concluded that it was an azo- compound, and represented it by the formula $C_6H_4<\genfrac{}{}{0pt}{}{CO.CH:CH.CO}{N=\!=\!=\!=N}>C_6H_4$, leucindigo being the corresponding hydrazo-compound $C_6H_4<\genfrac{}{}{0pt}{}{CO.CH:CH.CO}{NH\qquad HN}>C_6H_4$. In 1878 Sommaruga (*A.* 194, 107) proposed the formula



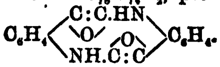
$$C_6H_4<\genfrac{}{}{0pt}{}{\genfrac{}{}{0pt}{}{O\text{———}O}{C=\!=\!=C}}{N:CH.CH:N}>C_6H_4$$

; in 1879 Baumann a. Tiemann suggested that indigo might be a derivative of diphenyl:



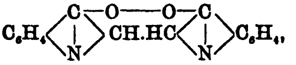
$$HC\genfrac{}{}{0pt}{}{C}{HN}H_3C_6.C_6H_3\genfrac{}{}{0pt}{}{C}{NH}CH \quad (O_2 \text{ bridging the two } C)$$

; whilst in 1882 Ljubavin (*B.* 15, 248, 728), regarding indigo as a substitution product of indoline $C_{16}H_{14}N_2$, proposed for it the formula:



$$C_6H_4<\genfrac{}{}{0pt}{}{C:C.HN}{NH.C:C}>C_6H_4$$

Baeyer's syntheses of indigo in 1882 from indoxyl and diisatogen (*B.* 15, 54) led him to conclude that it had the constitution



$$C_6H_4\genfrac{}{}{0pt}{}{C}{N}CH.HC\genfrac{}{}{0pt}{}{C}{N}C_6H_4$$

but his subsequent researches (*B.* 16, 2200; 17, 975) caused him to modify this formula to $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{CO}{HN}>C_6H_4$, representing it as the indogenide of ψ-isatin or diindogen. The latter formula which is now tolerably well established is based upon the following considerations: i. Indigo contains an NH group. ii. The carbon atoms are arranged in a line $C_6H_4.C.C.C.C.C_6H_4$, as follows from its formation from di-phenyl-diacetylene. iii. It can only be obtained from compounds in which the carbon atom directly united to the benzene nucleus is also united to O, or capable of becoming so united. iv. Its formation and properties indicate a close relationship to the β-indogenide of ethyl-ψ-isatin $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{CO}{C_6H_4}>NEt$, and to indirubine, which is proved to be the β-indogenide of ψ-isatin $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{CO}{C_6H_4}>NH$. The two latter bodies are formed by direct condensation of indoxyl $C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{NH}\gg CH$ with ethyl-ψ-isatin $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NEt}>CO$, or with isatin $C_6H_4<\genfrac{}{}{0pt}{}{CO}{N}\gg C(OH)$, in which reactions the indoxyl is probably first transformed into ψ-indoxyl $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>CH_2$, and the isatin into ψ-isatin

$C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>CO$. Combination then takes place between the α-carbon atom of the ψ-indoxyl and the β-carbon atom of the ψ-isatin, thus:

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>CH_2 + OC<\genfrac{}{}{0pt}{}{OC}{HN}>C_6H_4$$

$$= C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{CO}{C_6H_4}>NH.$$ Indigo is consequently the isomeric α-indogenide of ψ-isatin, though it cannot be formed from isatin and indoxyl owing to the greater tendency to reaction of the β-CO group.

Substitution products. **Indigo-mono-sulphonic acid** $C_{16}H_9N_2O_2(SO_3H)$. *Phœnicine-sulphuric acid.* Formed by allowing to stand for some time a mixture of indigo (1 pt.) with ordinary sulphuric acid (20 pts.), and separates as a blue powder on pouring the solution into water. It is easily soluble in alcohol, and in water free from acid, forming blue solutions. Its salts are sparingly soluble in water. In the dry state they are red, in solution blue.—A'Kaq: purple pp. (Crum, *Berz. J.* 4, 189; Berzelius, *Berz. J.* 4, 190; 7, 262; Dumas, *A.* 48, 340; Haeffely, *Gm.* 6, 462).

Indigo-di-sulphonic acid $C_{16}H_8N_2O_2(SO_3H)_2$. *Sulphindigotic acid. Cœruline-sulphuric acid. Indigo-extract.* Prepared by heating indigo with 15–20 pts. of ordinary, or better with 7–8 pts. of fuming, sulphuric acid. Amorphous blue solid. V. sol. water and alcohol. Completely removed from solution by wool or charcoal. The aqueous solution gives a continuous absorption spectrum (Vogel, *B.* 11, 1365). By oxidising agents it is converted into isatin sulphonic acid, by reducing agents into leucindigo-sulphonic acid. Its salts are mostly sparingly sol. water. The sodium salt (A''Na_2) appears in commerce under the name of *indigo-carmine* or *soluble-indigo* and is used for dyeing the so-called 'Saxony-blue' upon silk and wool.—A''K_2: amorphous blue coppery powder; S. (at 15°) = ·7.—A''Ba: m. sol. hot water (Crum, *Berz. J.* 4, 190; Berzelius, *Berz. J.* 7, 262; Dumas, *A.* 22, 72; Joss, *Berz. J.* 14, 316). According to Berzelius (*Gm.* 6, 435) there is formed, together with the di-sulphonic acid, another acid, the so-called '*indigo-hyposulphuric acid*,' which differs from the di-sulphonic acid in its ammonium salt being soluble in alcohol.

Indigo-di-carboxylic acid $C_{18}H_{10}N_2O_6$ *i.e.*

$$C_6H_3(CO_2H)<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{OC}{HN}>C_6H_3(CO_2H).$$

Prepared by warming nitro-benzaldehyde-carboxylic acid $C_6H_3(CHO)(NO_2)CO_2H$[1:2:4] with acetone and dilute NaOH. Also by reduction of *o*-nitro-phenyl-propiolic-carboxylic acid $C_6H_3(NO_2)(CO_2H).C{:}C.CO_2H$ with glucose and NaOH. Coppery blue powder. Insol. water, alcohol, ether, and chloroform. Dissolves in H_2SO_4 with a deep-blue colour, in alkalis with a bluish-green colour.—A''Ba.—$C_{18}H_6N_2O_6Ag_4$: insoluble.—A''Et_2: sublimes in prismatic tables, sl. sol. chloroform and benzene, nearly insol. alcohol and ether (Löw, *B.* 18, 950; *A.* 231, 365).

Di-chloro-indigo $C_{16}H_8Cl_2N_2O$. Obtained by the action of acetone and NaOH upon chloro-*o*-nitro-benzaldehyde (Müller, *German Patents* 30,329 and 33,064).

Tetra-chloro-indigo $C_{16}H_6Cl_4N_2O_2$ *i.e.*

$$C_6H_2Cl_2<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{OC}{HN}>C_6H_2Cl_2.$$ Obtained by the action of acetone and NaOH upon di-chloro-*o*-nitro-benzaldehyde [138°] (Bad. Anil. u. Soda-Fabrik, *G. P.* 32,238). Resembles indigo. Sublimes in violet-red vapours, condensing to blue coppery needles. Does not sulphonate or form a 'vat' so readily as ordinary indigo (Gnehm, *B.* 17, 753).

Di-bromo-indigo $C_{16}H_8Br_2N_2O_2$ *i.e.*

$$C_6H_3Br<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{CO}{NH}>C_6H_3Br.$$ Formed by adding bromo-isatin chloride (from bromo-isatin and PCl_5) to an excess of an 8 p.c. solution of HI in acetic acid (Baeyer, *B.* 12, 1315). Also obtained by boiling the acetyl derivative of tri-bromo-*o*-amido-acetophenone with Na_2CO_3 (Baeyer a. Bloem, *B.* 17, 968). Soluble in phenol, from which it separates on adding alcohol in small black needles. Nearly insol. alcohol, ether, acetic acid, or chloroform. Dissolves in conc. H_2SO_4 with a green colour. Sublimes in purple vapours. Forms a 'vat' like indigo. The absorption spectrum is the same as that of indigo.

Di-nitro-indigo $C_{16}H_8(NO_2)_2N_2O_2$ *i.e.*

$$C_6H_3(NO_2)<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{OC}{HN}>C_6H_3(NO_2).$$

Formed by adding nitro-isatin chloride (from nitro-isatin and PCl_5) to a solution of HI in acetic acid. Dark-red powder. Nearly insol. alcohol, ether, acetic acid, and chloroform; v. sol. phenol and hot nitrobenzene. The absorption spectrum is analogous to that of indigo. Dissolves in conc. H_2SO_4 with a violet-blue colour (Baeyer, *B.* 12, 1315).

Di-amido-indigo $C_{16}H_8N_2O_2(NH_2)_2$ *i.e.*

$$C_6H_3(NH_2)<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{OC}{HN}>C_6H_3(NH_2).$$

Formed by reduction of the foregoing nitro-compound with zinc-dust and acetic acid. Dark-blue pp. Nearly insol. alcohol, ether, and chloroform; v. e. sol. acetic acid with a pure blue colour. Its absorption spectrum is like that of indigo. It dissolves in dilute acids with a blue colour. It forms a 'vat' like indigo.

Di-benzoyl-indigo $C_{30}H_{18}N_2O_4$ *i.e.*

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{NBz}>C:C<\genfrac{}{}{0pt}{}{CO}{NBz}>C_6H_4$$ [108°]. Formed by heating indigo with BzCl. Brown amorphous powder. Insol. water and acetic acid, sl. sol. alcohol, m. sol. ether (Schwartz, *J.* 1863, 557).

Di-methyl-indigo $C_{16}H_8Me_2N_2O_2$ *i.e.*

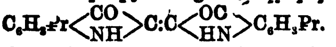
$$C_6H_3Me<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{OC}{HN}>C_6H_3Me.$$ Formed by the action of acetone and NaOH upon *o*-nitro-toluic aldehyde. Blue coppery powder. Sol. alcohol. Resembles ordinary indigo (Meister, Lucius a. Bruning, *G. P.* 21,683; *E. P.* 1882, 3,216).

ν-**Di-ethyl-indigo** $C_{20}H_{18}N_2O_2$ *i.e.*

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{NEt}>C:C<\genfrac{}{}{0pt}{}{OC}{EtN}>C_6H_4.$$ Prepared by reducing the di-ethyl derivative of ψ-isatine-ω-oxim $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NEt}>C(NOEt)$, with alcoholic ammonium sulphide, and then passing a stream of CO_2 through the solution. Blue felted needles; v. sol. alcohol, forming a deep-blue solution, the spectrum of which closely resembles that of indigo. Less soluble in ether, acetone, $CHCl_3$, CS_2, and aniline. It sublimes as a purple vapour,

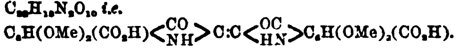
condensing to blue prisms. It dissolves in conc. H_2SO_4 with a greenish-blue colour, and on heating is sulphonated. With zinc-dust and alkalis it gives a vat. On oxidation it gives ethyl-ψ-isatin (Baeyer, *B.* 16, 2201).

Di-isopropyl-indigo $C_{22}H_{22}N_2O_2$ *i.e.*



$C_6H_3Pr{<}\begin{matrix}CO\\NH\end{matrix}{>}C{:}C{<}\begin{matrix}OC\\HN\end{matrix}{>}C_6H_3Pr$. Formed by the action of acetone and NaOH upon *o*-nitro-cuminic aldehyde $C_6H_3Pr(NO_2)CHO$ [4:2:1] (Einhorn a. Hess, *B.* 17, 2019). Also in small quantity from the dibromide of *o*-nitro-cumyl-acrylic acid $C_6H_3Pr(NO_2).CHBr.CHBr.CO_2H$ by heating with dilute NaOH and then adding glucose (Widman, *B.* 19, 261). Blue crystals with coppery lustre. Sol. alcohol, chloroform, and ether, insol. water. Shows the indigo spectrum. Sublimes in red vapours. Gives a 'vat.' Dissolves in cold conc. H_2SO_4 with a brown colour which on heating becomes green and finally blue.

Tetra-methoxy-indigo-di-carboxylic acid $C_{22}H_{18}N_2O_{10}$ *i.e.*

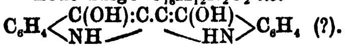


$C_6H(OMe)_2(CO_2H){<}\begin{matrix}CO\\NH\end{matrix}{>}C{:}C{<}\begin{matrix}OC\\HN\end{matrix}{>}C_6H(OMe)_2(CO_2H)$.

Obtained by the action of dilute aqueous NaOH and acetone upon nitro-opianic acid. Bluish-green solid. Sol. phenol and aniline with a green colour, insol. alcohol, benzene, chloroform, and acetone. Dissolves in hot dilute NH_3 with a blue colour, the solution showing the absorption spectrum of indigo-di-sulphonic acid. The solution of the NH_4 salt is precipitated by salts of Ca or Ba. It dissolves unaltered in conc. H_2SO_4 with a violet-blue colour. On heating it evolves violet vapours and a smell of vanillin (Liebermann, *B.* 19, 352).

Allied compounds.

Leucindigo $C_{16}H_{12}N_2O_2$ *i.e.*



$C_6H_4{<}\begin{matrix}C(OH){:}C.C{:}C(OH)\\NH\diagup\quad\diagdown HN\end{matrix}{>}C_6H_4$ (?).

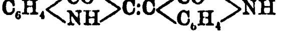
Indigo-white. Formed by reduction of indigo by means of alkaline reducing agents such as $FeSO_4$ and lime, orpiment and NaOH, glucose and NaOH, sodium hydrosulphide, &c. Indigo (½ kilo.) is allowed to stand for one or two days with a mixture of lime and $FeSO_4$ in a closed vessel of 100 litres' capacity, filled with water. The clear liquor is then siphoned off into another vessel, filled with CO_2, and HCl is added. The ppd. leucindigo is then dried in a stream of CO_2 or H (Dumas, *A.* 48, 257; Ullgren, *A.* 136, 96). Greyish-white silky solid. Sol. alcohol and ether, insol. water. Dissolves in alkalis and behaves like a weak acid. By exposure to air it is quickly oxidised to indigo. By heating with zinc-dust and aqueous $Ba(OH)_2$ at 180° it yields indoline. On distilling with zinc-dust it gives indole and scatole (Baeyer, *B.* 15, 54).

Leucindigo-sulphuric acid. *Indigo-white-sulphuric acid.* The potassium salt is obtained by shaking damp pressed leucindigo (25 g.) dissolved in 25 g. of aqueous KOH(1:2) with 12–15 g. of $K_2S_2O_7$. The solution is diluted with an equal bulk of water exposed to the air, filtered from indigo, shaken with ether, and freed from potassium sulphate by mixing with six times its volume of absolute alcohol (Baeyer, *B.* 12, 1600; Baumann a. Tiemann, *B.* 13, 411). By the action of air or $FeCl_3$ it is oxidised to indigo. The solution of the K salt is resolved by dilute acids into leucindigo and H_2SO_4. This compound was regarded by Baeyer as identical with 'indoxyl-sulphuric acid,' but according to Baumann and Tiemann this is not the case.

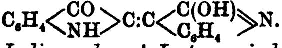
Indican $C_{26}H_{31}NO_{17}$ (?). *Plant indican. Glucoside of indigo or leucindigo.* Occurs in the *Indigofera*, in *Isatis tinctoria* (woad), *Polygonium tinctorium*, *Bletia tankervilliæ*, *Callanthi veratrifolia*, and other plants (Schunck, *J.* 1885, 659; 1858, 465; *C. N.* 37, 223). Prepared by extracting dried and powdered woad leaves with cold alcohol. The extract treated with a little water is evaporated at the ordinary temperature of the air, the aqueous residue shaken with CuO, filtered, freed from copper by H_2S, filtered, and again evaporated in the cold. The syrup is taken up with alcohol, precipitated with twice its volume of ether, and the filtrate evaporated at the ordinary temperature. Light-brown syrup. Slightly bitter taste. Sol. water and alcohol. In alcoholic solution it gives a yellow pp. with lead acetate. Boiled with KOH it evolves NH_3. By long boiling with water it is decomposed. It is decomposed by baryta water in the cold with formation of a syrupy body called *indicanine* $C_{20}H_{23}NO_{12}$ (?). By heating with dilute acids it is resolved into *indigo* and *indiglucin* (a sugar). Simultaneously are formed *indirubin* $C_{16}H_{10}N_2O_2$, *indiretin* $C_{18}H_{17}NO_5$ (dark-brown resin, sol. alcohol), *indifulvin* (reddish-yellow resin, insol. alkalis), *indihumin* $C_{10}H_9NO_3$ (brown powder, insol. water and alcohol, sol. alkalis), *indifuscin* $C_{24}H_{20}N_2O_9$ (analogous to inhumin), acetic acid, formic acid. and CO_2 (Schunck a. Römer, *B.* 12, 2311; *C. N.* 39, 119). When fresh indican solution is mixed with strong acid and boiled, only indigo and indiglucin are obtained, but if the indican solution is previously boiled for a short time indirubin is also formed (Schunck, *C. J.* 35, 528).

The name '*indican*' has also been erroneously given to indoxyl-sulphuric acid which is a normal constituent of the urine of animals (Baumann a. Tiemann, *B.* 12, 1098; 13, 411).

Indirubin $C_{16}H_{10}N_2O_2$ *i.e.*



$C_6H_4{<}\begin{matrix}CO\\NH\end{matrix}{>}C{:}C{<}\begin{matrix}CO\\C_6H_4\end{matrix}{>}NH$ or



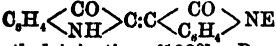
$C_6H_4{<}\begin{matrix}CO\\NH\end{matrix}{>}C{:}C{<}\begin{matrix}C(OH)\\C_6H_4\end{matrix}{\gg}N$. *Indipurpurin. Indigo-red. ψ-Isatine-α-indogenide.* Formed together with indigo when a solution of indican, previously boiled for a short time, is treated with an acid. Also together with indigo by the action of zinc-dust and acetic acid upon isatin chloride. Obtained synthetically by condensation of isatin and indoxyl:—An indoxyl solution prepared by boiling 1 pt. of indoxylic acid in 100 pts. of water for a short time is filtered into a solution of ¾ pt. of isatin in 200 pts. of boiling water. Na_2CO_3 is added and the precipitated indirubin is filtered off and washed. Needles. Sol. alcohol, ether, benzene, and acetic acid forming purple solutions; insol. water. Begins to sublime at 140°, condensing in fine reddish needles (Schunck, *C. J.* 37, 617). Gives an absorption spectrum which is different from that of indigo. Forms a 'vat.' Is more stable towards oxidising agents than indigo. By zinc-dust and acetic acid it is reduced first to leucindirubin $C_{16}H_{12}N_2O_2$ and finally to indileucin $C_{16}H_{12}N_2O$ (Schunck, *B.* 12, 1220; *C. N.* 39, 119; Baeyer, *B.* 12, 457; 14, 1745; 15, 50; 16, 2200).

The *bromo- derivative* $C_{16}H_9BrN_2O_2$ from indoxyl and bromisatin resembles indirubin.

The *di-bromo- derivative* $C_{16}H_8Br_2N_2O_2$ is obtained in very small quantity together with dibromoindigo by reduction of bromisatin chloride with HI. Needles: sol. alcohol and ether (Baeyer, *B.* 12, 1315).

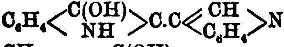
The *di-nitro- derivative* $C_{16}H_8(NO_2)_2N_2O_2$ is formed in small quantity together with nitroindigo by reduction of nitroisatin chloride with HI. Sol. alcohol with a red colour.

Ethyl-indirubin $C_{18}H_{14}N_2O_2$ *i.e.*

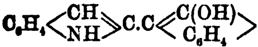


$\mathrm{C_6H_4{<}\substack{CO\\NH}{>}C{:}C{<}\substack{CO\\C_6H_4}{>}NEt}$. *α-Indogenide of ethyl-ψ-isatin.* [198°]. Prepared by adding a hot aqueous solution of indoxyl to a hot aqueous solution of ethyl-ψ-isatin mixed with HCl; brownish-red needles of the product separate at once (Baeyer, *B.* 16, 2200). Coppery needles: sol. chloroform to a red solution, sl. sol. alcohol and acetone. Dissolves in conc. H_2SO_4 with a brown colour which becomes violet on heating with formation of a sulphonic acid. It gives a 'vat' with zinc-dust and alkalis.

Indileucin $C_{16}H_{12}N_2O$ *i.e.*

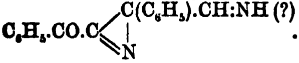


$\mathrm{C_6H_4{<}\substack{C(OH)\\NH}{>}C.C{\lessdot}\substack{CH\\C_6H_4}{>}NH}$ or



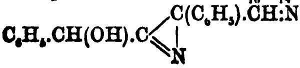
$\mathrm{C_6H_4{<}\substack{CH\\NH}{\gtrdot}C.C{\lessdot}\substack{C(OH)\\C_6H_4}{>}NH}$. Obtained by reduction of indirubin with zinc-dust and acetic acid; the yield is 35 p.c. Colourless glistening needles; sol. acetic acid, sl. sol. alcohol, ether, benzene, and chloroform. Fe_2Cl_6 gives an intense yellowish-green colour. Nitrous acid colours the acetic acid solution orange. Picrate $C_{16}H_{12}N_2OC_6H_2(NO_2)_3OH$: orange crystals. Methyl ether $C_{16}H_{11}N_2(OMe)$: [192°]; large glistening prisms; sol. alcohol and ether. Triacetyl derivative $C_{16}H_9Ac_3N_2O$: [278°]; flat yellow needles (Forrer, *B.* 17, 977).

Iso-indileucin $C_{16}H_{12}N_2O$ *i.e.*



$\mathrm{C_6H_5.CO.C}\begin{array}{l}\diagup \mathrm{C(C_6H_5).CH{:}NH\ (?)}\\ \quad |\\ \diagdown\!\!\diagdown \mathrm{N}\end{array}$. [192°]. Formed by shaking a benzene solution of ω-di-bromo-acetophenone $C_6H_5.CO.CHBr_2$ with strong aqueous NH_3. Yellow plates. Sol. hot alcohol, insol. water, and cold benzene. Weak base. It gives a splendid red colouration on the addition of phenol to its H_2SO_4 solution. By reduction in alcoholic solution with tin and HCl it yields hydroisoindileucin. Picrate $C_{16}H_{12}N_2OC_6H_2(NO_2)_3OH$ aq: [150°]; yellow needles (Engler a. Hassenkamp, *B.* 18, 2241).

Hydro-iso-indileucin $C_{16}H_{14}N_2O$ *i.e.*

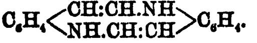


$\mathrm{C_6H_5.CH(OH).C}\begin{array}{l}\diagup \mathrm{C(C_6H_5).CH{:}NH\ (?)}\\ \quad |\\ \diagdown\!\!\diagdown \mathrm{N}\end{array}$ [160°] with decomposition. Formed by the action of tin and HCl on an alcoholic solution of isoindileucin. Plates. V. sol. alcohol, ether, and $CHCl_3$. Sol. H_2SO_4 with a blue colour. Oxidised back to isoindileucin by treatment with CrO_3.

Methyl-iso-indileucin $C_{16}H_{11}MeN_2O$. [115°]. Formed by heating isoindileucin with MeI, and alcoholic KOH at 100°-110°. Plates. Sol. alcohol and ether. No colouration with H_2SO_4 and phenol (Engler a. Hassenkamp, *B.* 18, 2242).

Indoin $C_{32}H_{20}N_4O_5$. Formed by adding $FeSO_4$ to a solution of *o*-nitro-phenyl-propiolic acid in H_2SO_4, or by the action of the propiolic acid on an H_2SO_4 solution of indoxyl. Also by action of $FeSO_4$ and conc. H_2SO_4 upon *o*-di-nitro-di-phenyl-diacetylene $C_6H_4(NO_2).C{:}C.C{:}C.C_6H_4(NO_2)$ or upon the isomeric diisatogen $C_{16}H_8N_2O_4$; and by treatment of isatogen-sulphurous acid with conc. H_2SO_4. Blue dye-stuff, resembling indigo in many points. Dissolves in cold H_2SO_4 with a blue colour, but is not readily sulphonated. Also dissolves to a blue solution in cold aniline or aqueous SO_2. Combines with SO_2. Gives a 'vat' (Baeyer, *B.* 14, 1742; 15, 52, 57, 212).

Indoline $C_{16}H_{14}N_2$ *i.e.*



$\mathrm{C_6H_4{<}\substack{CH{:}CH.NH\\NH.CH{:}CH}{>}C_6H_4}$. *Diindole.* [245°]. Formed by heating leucindigo (indigo-white) (1 pt.) with barium hydrate (2 pts.), zinc-dust (1½ pts.) and water (180 pts.) for 24 hours at 180° (Schützenberger, *J.* 1877, 511); the product is extracted with alcohol, the alcohol evaporated, and the residue heated with zinc-dust when indoline sublimes. More readily obtained by reduction of flavindine dissolved in dilute NaOH, with 3 p.c. sodium amalgam (Giraud, *J.* 1880, 586). Long yellow needles by sublimation. Sol. alcohol and ether with a blue fluorescence, insol. water. Forms salts with acids. The picrate $C_{16}H_{14}N_2C_6H_2(NO_2)_3OH$ is sl. sol. alcohol.

Di-chloro-indoline $C_{16}H_{12}Cl_2N_2$. Got by passing Cl into a $CHCl_3$ solution of indoline.

Di-nitro-indoline $C_{16}H_{12}(NO_2)_2N_2$. Got by dissolving indoline in warm nitric acid. Crystallises from alcohol in orange-yellow crystals.

Indoline-di-sulphonic acid $C_{16}H_{12}(SO_3H)_2N_2$ is formed by heating indoline with fuming H_2SO_4 at 180°. Its sodium salt $A''Na_2$ is crystalline.

Other references.—Sommaruga, *B.* 11, 1085; Einhorn, *B.* 16, 2208; Alexejew, *B.* 17, Ref. 172; *Bl.* 42, 320; Müller, *A.* 212, 122; Kolbe, *J. pr.* [2] 30, 84; Rosenstiehl, *A. Ch.* [5] 21, 286; *C. J.* 40, 98. *V.* also ISATIN, ISATIC ACID, OXINDOLE, INDOXYL, INDOXYLIC ACID, DIISATOGEN, INDOGENIDES, INDINE, INDOLE, NITRO-PHENYL-PROPIOLIC ACID, DI-NITRO-DI-PHENYL-DI-ACETYLENE, ISATOGENIC ACID.

A. G. G.

END OF THE SECOND VOLUME.

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